ABSTRACT

Title of Dissertation:	APPLIED PHOTOCHEMISTRY FOR MULTICOLOR PHOTOLITHOGRAPHY
	Steven Michael Wolf, Doctor of Philosophy, 2019
Dissertation directed by:	Professor Daniel E. Falvey Department of Chemistry and Biochemistry

Photolithography is the most mature technique for nanomanufacturing. Traditional photolithography generates patterns using a single wavelength of light. Recently, there has been considerable interest in the development of new photoinitiators that can improve the patterning process by incorporating multiple wavelengths of light. This text will focus specifically on organic photoinitiators.

Chapter 1 will begin with an introduction to organic photochemistry and the description of laser flash photolysis, a time-resolved UV-Vis spectroscopy technique used for characterizing short-lived intermediates formed as a result of photolysis. Then, it will provide a description of photolithography and explore the limitations of current techniques. Finally, it will describe multicolor photolithography and the characteristics of a multicolor photoinitiator.

Chapters 2-4 will explore various organic compounds that have been investigated as potential multicolor photoinitiators. Chapter 2 will focus on the

photodecomposition of α-diketones into radicals that can be used to initiate polymerization of sytrenic monomers. Laser flash photolysis, product analysis, and computational modeling will be used to demonstrate that this decomposition occurs through a Norrish type I mechanism where higher excited states are populated via triplet-triplet annihilation. Chapter 3 will explore dithioesters and trithiocarbonates that can be used as initiators for reversible addition-fragmentation chain transfer (RAFT) polymerization. Dithioesters and trithiocarbonates have a long history in the literature but their potential as photoinitiators has not been explored in depth. In chapter 3, computational modeling is used to investigate the excited states of various RAFT agents. Chapter 4 will focus on 2-methoxy-9,10-dioxo-9,10-dihydroanthracen-1-yl 4-methylbenzenesulfonate, a multicolor photoacid generator (PAG). When irradiated with 355 nm light, this PAG releases *p*-toluenesulfonic acid which can be used to initiate cationic polymerization. The addition of 532 nm light accelerates the acid release, making the PAG a two-color photoinitiator. Multicolor PAGs provide improved resolution over one-color systems which makes them useful for photolithography and nanomanufacturing.

APPLIED PHOTOCHEMISTRY FOR MULTICOLOR PHOTOLITHOGRAPHY

by

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Dedication

This research is dedicated to my friends and family. It wouldn't have happened without your support.

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Table of Contents

List of Tables

List of Figures

Chapter 2: Triplet-Triplet Annihilation of α-Diketones

Chapter 3: Photophysics of Dithioesters and Trithiocarbonates

Chapter 4: Photogeneration of Acids by Direct Irradiation of 2-methoxy-9,10-dioxo-9,10-dihydroanthracen-1-yl 4-methylbenzenesulfonate

List of Schemes

Chapter 1: Organic Photochemistry

Chapter 2: Triplet-Triplet Annihilation of α-Diketones

Chapter 3: Photophysics of Dithioesters and Trithiocarbonates

List of Abbreviations

ATR	Attenuated total reflectance
B3LYP	Becke, three-parameter, Lee-Yang-Parr functional
BDE	Bond dissociation energy
CAM	Coulomb-attenuating method
CHD	1,4-cyclohexadiene
CW	Continuous wave
DART	Direct analysis in real time
DCM	Dichloromethane
DFT	Density functional theory
DNQ	Diazonaphthaquinone
EUV	Extreme ultraviolet
FID	Flame ionization detection
FT-IR	Fourier transform infrared spectroscopy
G3	Gaussian-3 procedure
GC	Gas chromatography
LFP	Laser flash photolysis
M062X	Minnesota 06 functional with double the amount of nonlocal exchange
MAE	2-methoxyanthraquinone esters
MeCN	Acetonitrile
MeOH	Methanol
MN12SX	Minnesota 12 functional with screened exchange
MP2	Møller-Plesset correlation energy correction, second-order
Nd:YAG	Neodymium-doped yttrium aluminum garnet laser
NMR	Nuclear magnetic resonance
OD	Optical density
PAG	Photoacid generator
PBE0	Perdew, Burke, and Ernzerhof functional
p-TsOH	*p*-toluenesulfonic acid
RAD	Radical thermochemistry procedure
RAFT	Reversible addition-fragmentation chain transfer
TD-DFT	Time-dependent density functional theory
TEA	Triethylamine
TEMPO	(2,2,6,6-tetramethylpiperidin-1-yl)oxyl
TTA	Triplet-triplet annihilation
TTA-UC	Triplet-triplet annihilation-upconversion
UV	Ultraviolet
Vis	Visible

Chapter 1: Organic Photochemistry

1.1 Introduction to Organic Photochemistry

In the broadest terms, organic photochemistry is the field of organic chemistry that makes use of light as a reagent. While organic photochemistry is sometimes thought of as a recent development, the first photochemical reaction observed for an organic molecule dates back to 1834 when Trommsdorff described the reaction of α-santonin in sunlight.[1–3] This reaction was later determined to result in the formation of lumisatonin.[4,5] Nearly fifty years later, Ciamician published his first investigations into the chemical actions of light. Ciamician would go on to publish forty notes and nine memoirs on the topic of photochemistry between 1900 and 1915.[6–8] At this time, organic photochemistry was considered unpredictable due to the seemingly random nature of the reactions observed. As a result, photochemical research would endure a prolonged period of disinterest before experiencing a renaissance in the early 1960s with the work of Zimmerman.[9–12] Zimmerman proposed that the forces that governed ground state reactions were also at work in the excited state and that, rather than reacting randomly, photochemical reactions proceeded through continuous electron redistribution and thus could be described logically using arrow pushing.[13] Since this so-called "golden age" of photochemistry, the field has grown to encompass a variety of applications such as fundamental investigation into excited state chemistry,[14–17] synthesis,[18–27] nanomanufacturing,[28] and the development of photoremovable protecting groups.[29–38] This text will focus on the use of photochemical reactions for the purposes of multicolor photolithography.

1.2 Laser Flash Photolysis

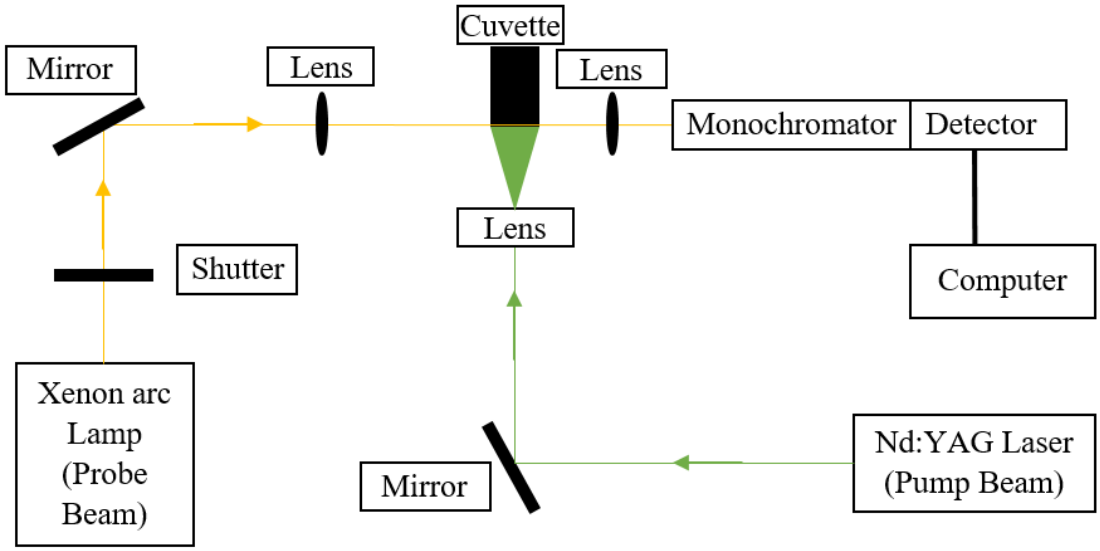
Throughout this text, a technique known as laser flash photolysis (LFP) will be used for mechanistic investigation of photochemical reactions. LFP is a time resolved UV-Vis spectroscopy technique used for kinetic studies involving transient species.[39,40] LFP uses a pump beam to generate a large concentration of short-lived intermediates (i.e. triplets, radicals, etc.) combined with a fast detection system to characterize the transient species. This allows for spectroscopic analysis of light-generated intermediates in photochemical reactions. Spectra obtained from LFP can be used to identify these intermediates and provide valuable information about transitions to higher excited states and lifetimes.

The excitation beam used for LFP experiments in this text is the third (355 nm) or forth (266 nm) harmonic of a neodymium-doped yttrium aluminum garnet laser ($Nd:Y_3Al_5O_{12}$, Nd:YAG). The pulse width of the excitation beam was 4-6 ns. The probe beam used was a 350 W Xenon arc lamp that is shuttered in sync with the laser pulses. A monochromator is used to select the wavelength for monitoring. The signal is then amplified by a photomultiplier tube and measured using an oscilloscope. The raw voltage measured by the oscilloscope is converted into optical density change (ΔOD) using computer software (Scheme 1.1).

A positive ΔOD indicates that the excited state or intermediate generated by the pulse beam has a greater absorbance than the ground state. A negative ΔOD is indicative of a bleaching event where the excited state absorbs less light from the probe beam than the ground state. The ΔOD for a given wavelength can be measured as function of time and plotted to give a waveform. Waveforms can be collected for

multiple wavelengths then used to assemble a transient absorption spectrum. Transient absorption spectra can be used to characterize short-lived intermediates by comparison to known spectra. Reactivity of excited states can also be determined by monitoring signal changes in the presence of quenchers, donors, or other reagents.

Scheme 1.1 – Layout of a laser flash photolysis system.



1.3 Photolithography and Photoresists

Photolithography is the most mature technique for nanomanufacturing. Traditional photolithography involves using light to introduce a pattern onto a substrate. To achieve this pattern transfer, the substrate is first coated in a photoactive layer known as a photoresist. There are two types of photoresist; positive- and negative-tone.[41]

A positive-tone photoresist is a material that is sparingly soluble or insoluble in a developing solvent, but becomes more soluble when irradiated. The most common example of a positive-tone resist is the novolac resin.[42–44] Novolac resins are the product of a condensation reaction of phenol (or a substituted phenol) with formaldehyde to form a polymer. This polymer is then impregnated with

diazonaphthoquinone (DNQ). By itself, DNQ inhibits novolac dissolution. Once irradiated however, DNQ undergoes a highly exothermic Wolff rearrangement yielding a ketene. This ketene is rapidly hydrolyzed to form indene carboxylic acid. The combination of increasing local temperature and production of organic acid promotes the degradation of the novolac's phenolic strings. The breakdown of the resin has the effect of enhanced solubility in exposed regions allowing the irradiated portion of the novolac to be removed in a development step. The substrate and remaining photoresist are then plasma etched to remove the normal pattern of irradiation to the substrate (i.e. the positive image of the light).

A negative-tone photoresist is typically a viscous liquid that can be made solid when irradiated. A common example of a negative-tone resist is polymerizable alkenes such as styrenics and acyrlates.[45,46] The resist includes a photoinitiator (and often a co-initiator) that is capable of forming radicals to initiate polymerization. Upon irradiation, the initiator produces radicals and creates polymer in the exposed regions. Another common form of negative-tone photoresist is an epoxide containing resin and a photoacid generator (PAG).[47,48] In such cases, the photoacid generator absorbs light and creates a strong acid that can protonate the epoxide. Once protonated, the epoxides are susceptible to nucleophilic addition, initiating polymerization. Propagation operates when an alcohol (formed by the opening of an epoxide) adds to a protonated epoxide. Termination is typically caused by water or a byproduct from the photoacid generator. In both cases, the polymer that is formed is much less soluble than the monomers and remains on the substrate after development. During etching the inverse pattern of irradiation is transferred to the substrate hence the resist is known as "negative-tone."

Traditionally, both positive- and negative-tone photoresists use a single wavelength of light. The next section of this chapter will outline a multi-wavelength scheme.

1.4 Multicolor Photolithography

Industrial photolithography typically uses one-color photolithography, often extreme ultraviolet (EUV), to excite a photoinitator in a negative-tone photoresist. In these one-color schemes, select regions of the photoresist are illuminated with the chosen wavelength to generate an excited state that can initiate polymerization (Scheme 1.2 – A). Due to diffraction, features formed by using one-color photolithography can only be made as small as a quarter of the wavelength used for exposure.[49] Transverse resolution (the shortest distance between printable features) is also limited by diffraction. The limit is often described using the Abbe criterion (Equation 1.1), which defines transverse resolution (d) as a function of wavelength (λ) and numerical aperture (NA). The NA is the product of the refractive index (n) of the medium and the sine of the half-angle of the beam (Equation 1.2). These diffraction limits dictate that, for a one-color scheme, smaller features and resolutions can only be achieved using shorter wavelengths. Current practices have implemented wavelengths as low as 13.5 nm. Unfortunately, generation of such wavelengths is costly and longer, more inexpensive wavelengths would be preferred.[49,50]

$$d = \frac{\lambda}{2NA} \qquad (Equation\ 1.1)$$

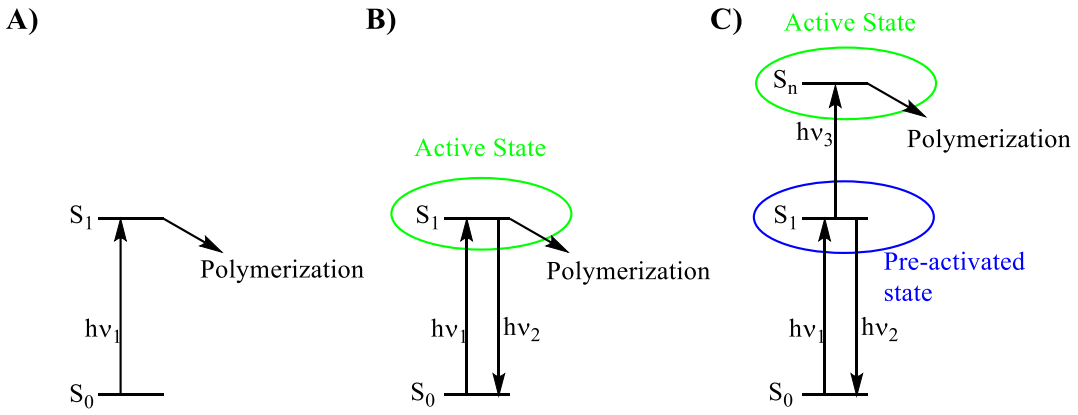
$$NA = n * \sin(\theta) \qquad (Equation\ 1.2)$$

New techniques for photolithography have been developed to escape the limitations imposed by diffraction. One such technique is the one-color scheme known as two-photon absorption where two photons are absorbed simultaneously. In two-photon absorption schemes, the rate of polymerization is proportional to the square of the laser power. Thus, when the laser intensity for the exposure beam is adjusted to be close to the polymerization threshold for the photoresist, only the inner region of the exposure (where, assuming a Gaussian profile, laser intensity is greatest) has a photon density sufficient for simultaneous two-photon absorbance. In this way, two-photon absorption allows for pattern fabrication in a regime outside of the conditions governed by the Abbe criterion. Using this technique Duan et al. report fabricated features as small as $\lambda/10$ and Fourkas et al. report features as small as $\lambda/20$.[49,51]

A related two-photon technique takes its inspiration from the field of microscopy. Stimulated emission depletion microscopy, a Nobel Prize-winning microscopy technique, improves imaging resolution by adding a second wavelength of light to deplete the initial excited states that are formed, deactivating chemistry in a specific region.[52,53] The analogous photolithography technique seeks to use two-colors (rather than two photons of the same color) to enhance fabrication resolution. In these two-color schemes, the photoinitiator is excited with one color of light ($h\nu_1$) to a radical-forming active state (Scheme 2.1 – B). From this state, deactivation also occurs with the second color ($h\nu_2$). Because deactivation is not 100% efficient, some polymerization can occur in the area between features. Still, features as small as 9 nm have been manufactured using a two-color approach.[54,55]

The generation of even smaller features may be possible by the incorporating of a third wavelength of light.[55–58] In the three-color scheme, the first color of light ($h\nu_1$) excites the photoinitiator molecule to the "pre-activated" state. Unlike the active state in two-color approaches, this "pre-activated" state cannot lead to polymerization on its own and molecules in this state can only relax thermally back to the ground state. However, a second color ($h\nu_2$) can also be used to stimulate the return to the ground state. The "pre-activated" state can also be further excited by a third color of light ($h\nu_3$) promoting the remaining molecules to the "active" state. The "active" state then initiates polymerization reactions (Scheme 1.2 – C). This text will explore three types of photoinitiators (α-diketones, reversible addition-fragmentation chain transfer agents, and 2-methoxy-9,10-dioxo-9,10-dihydroanthracene-based photoacid generators) and their capacity for multicolor-photolithography.

Scheme 1.2 – Energy level diagram for photoinitiators in a single color approach (A), a two-color approach (B), and a three-color approach (C).



Chapter 2: Triplet-Triplet Annihilation of α-Diketones

2.1 Background on Biacetyl

Development of new photoinitiators is a topic of current interest.[59–63] Ideally, a photoinitiator must be able to absorb light and initiate polymerization while remaining non-reactive toward monomers in the dark. Additionally, it would be preferable if the photoinitiator was commercially available, inexpensive, and non-toxic. In an attempt to meet these standards, biacetyl, **1a**, was investigated as a photoinitiator. In addition to the aforementioned characteristics, **1a** also possesses an attractive absorption spectrum extending into the visible region (Figure 2.1). Visible light absorption allows for polymerization without the need for expensive and technologically challenging extreme ultraviolet (EUV) radiation.

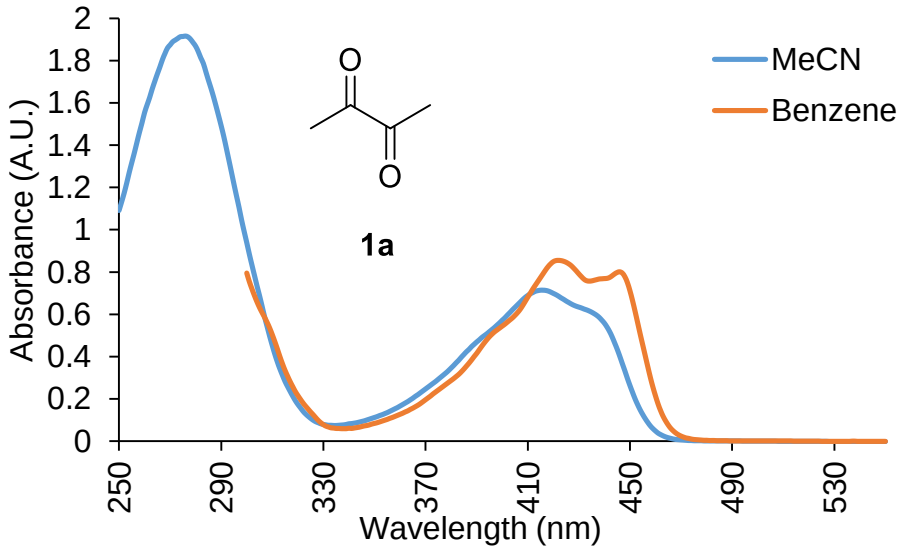
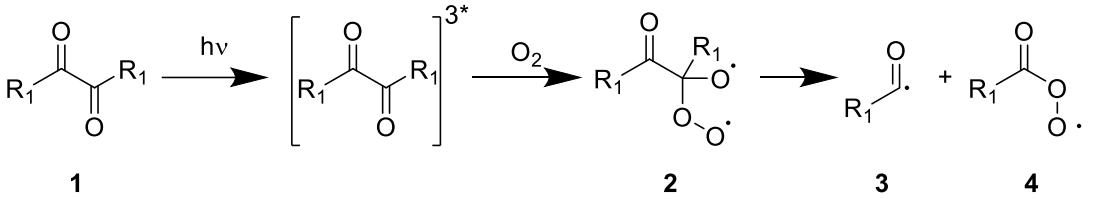


Figure 2.1 – Absorbance of **1a** in acetonitrile (MeCN) and benzene.

1a is one of the simplest α-diketones and has been studied extensively.[64–69] Like other α-diketones, **1a** is expected to react with atmospheric oxygen to ultimately form acyl radicals, **3**, and acylperoxyl radicals, **4** (Scheme 2.1). Though these radicals could

potentially initiate polymerization, they are not made efficiently and the acylperoxyl radicals form epoxides from olefins instead.[70–75]

Scheme 2.1 – Formation of acyl radicals via the reaction of α-diketones with oxygen.[70,73]



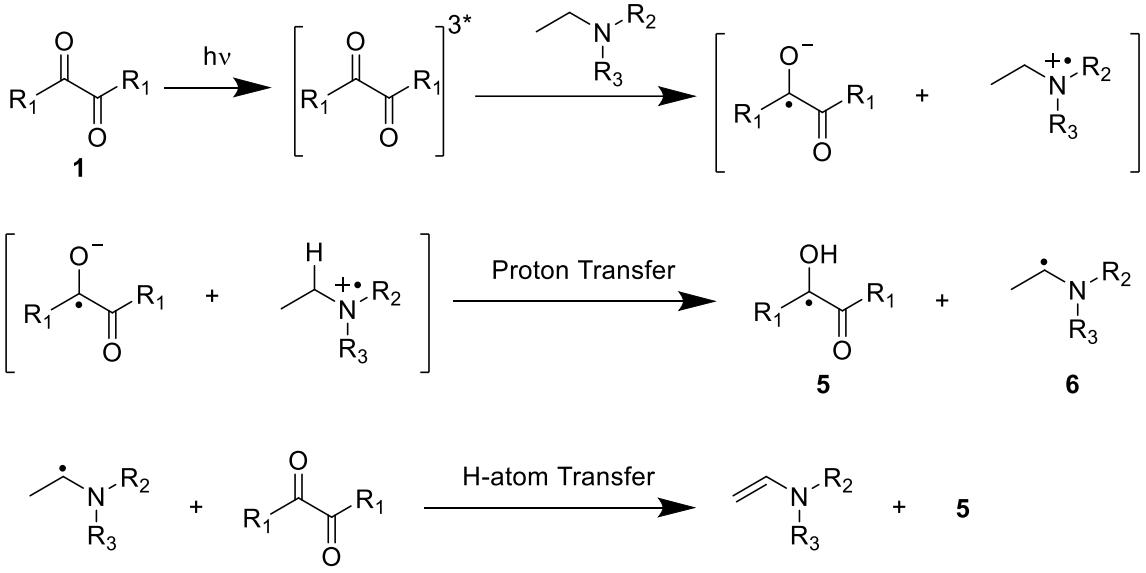
To improve radical formation and polymerization efficiency, α-diketones are typically used in the presence of a co-initiator.[76–78] Often, amines such as triethylamine are used as co-initiators.[79,80] In a co-initiated system, the excited α-diketone is reduced by a single electron transfer from the amine co-initiator resulting in a contact radical ion pair. The α-diketone radical anion then abstracts a proton from the amine radical cation to form a ketyl radical, **5**, and an α-amine radical, **6**. **6** undergoes a hydrogen atom transfer with a ground state α-diketone generating an additional ketyl radical (**5**) and an enamine byproduct (Scheme 2.2). Ketyl radicals proceed to initiate polymerization.[81]

Additionally, α-diketones have been shown to undergo photochemical reactions when excited by multicolor irradiation. McGimpsey and Scaiano have demonstrated the ability to make benzoyl radicals from aryl α-diketones via sequential excitation with two different wavelengths.[82] The α-diketone absorbs the first photon (308 nm), ultimately populating its lowest triplet excited state. The triplet state can then absorb a second photon (517 nm) that further excites the α-diketone to an excited state that generates radicals. The ground state α-diketone is transparent at 517 nm but the excited state absorbs strongly at that wavelength, allowing for sequential excitation. Using this

method of generating benzoyl radicals, McGimpsey and Scaiano are able to observe crossover products when irradiating different aryl α-diketones simultaneously. Burland and coworkers use **1a** in a polycyanoacrylate matrix as a two-photon material for holography.[68,83,84] Their system uses two different wavelengths of light (457.9 nm and 752.5 nm) to populate higher triplet states. Although Burland et al. report that the exact process is not known, they are able to distinguish it from the hydrogen atom abstraction chemistry of the lowest triplet thereby ruling out a strictly one-photon process.[83]

This chapter will demonstrate that the photolysis of **1a** in the absence of oxygen and co-initiators leads to the formation of acyl radicals. Computational results will show that the lowest triplet of **1a** does not possess sufficient energy to effect a cleavage of the central C-C bond yet steady-state photolysis results will indeed show decomposition of **1a**. This is attributed to a triplet-triplet annihilation mechanism.

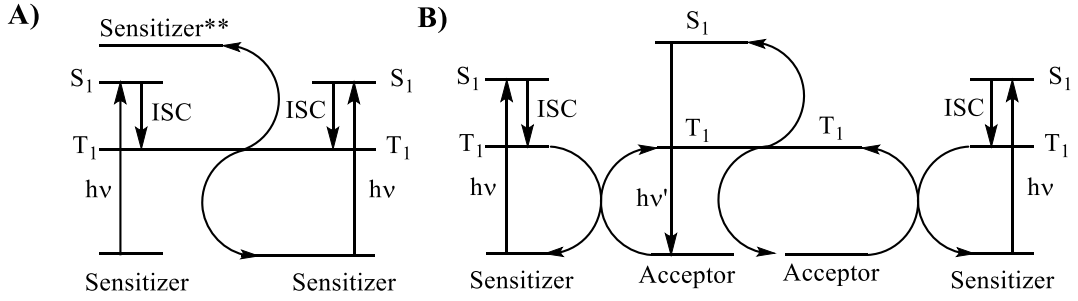
Scheme 2.2 – Generation of ketyl radicals from α-diketones in the presence of an amine co-initiator.[79–81]



2.2 Triplet-Triplet Annihilation

Triplet-triplet annihilation (TTA) is a well-known mechanism for accessing high energy intermediates.[85,86] TTA is typically composed of three main steps. The first step is absorption, where a sensitizer absorbs a photon and enters its excited singlet state. The second step is intersystem crossing, which generates a triplet excited state. Finally, when two triplet molecules come collide, one molecule becomes further excited and forms a high-energy intermediate while the other molecule returns to the ground state (Scheme 2.3 – A). TTA is regularly used as a method for photon upconversion in solar cells. Triplet-triplet annihilation-upconversion (TTA-UC) pairs a sensitizer and an acceptor molecule to generate a photon with a shorter wavelength (hν') than the excitation wavelength (hν). Like more general triplet-triplet annihilation, TTA-UC begins with absorption of a photon by the sensitizer and intersystem crossing to generate a triplet excited state. Then, an energy transfer occurs from the excited sensitizer to the acceptor to generate excited triplet acceptor. Two triplet acceptors can then annihilate to generate one excited singlet acceptor and one ground state acceptor. The singlet acceptor then fluoresces producing hypsochromically shifted photons (Scheme 2.3 – B).

Scheme 2.3 – Triplet-triplet annihilation (A) and triplet-triplet annihilation-upconversion (B).



*2.3 Photochemistry of **1a***

1a has a weak n-pi* absorption band in the visible region (c. 420 and 445 nm) making **1a** a potential visible light photoinitator. To investigate the photophysics of **1a**, 0.8% v/v solutions of **1a** were photolyzed in various solvents using a 447 nm continuous wave (CW) diode laser with a variable power output. Experiments began in benzene, as it is an inert solvent that does not participate in H-atom transfer or electron transfer with the excited **1a**. Experiments were monitored via absorption spectroscopy. Throughout the course of the reaction, it was observed that **1a** decomposition occurs readily in the absence of a co-initiator (Figure 2.2). The depletion was significant to the extent that, after thirty minutes of photolysis, the visible n-pi* absorption band was completely abolished with an observable isosbestic point c. 360 nm.

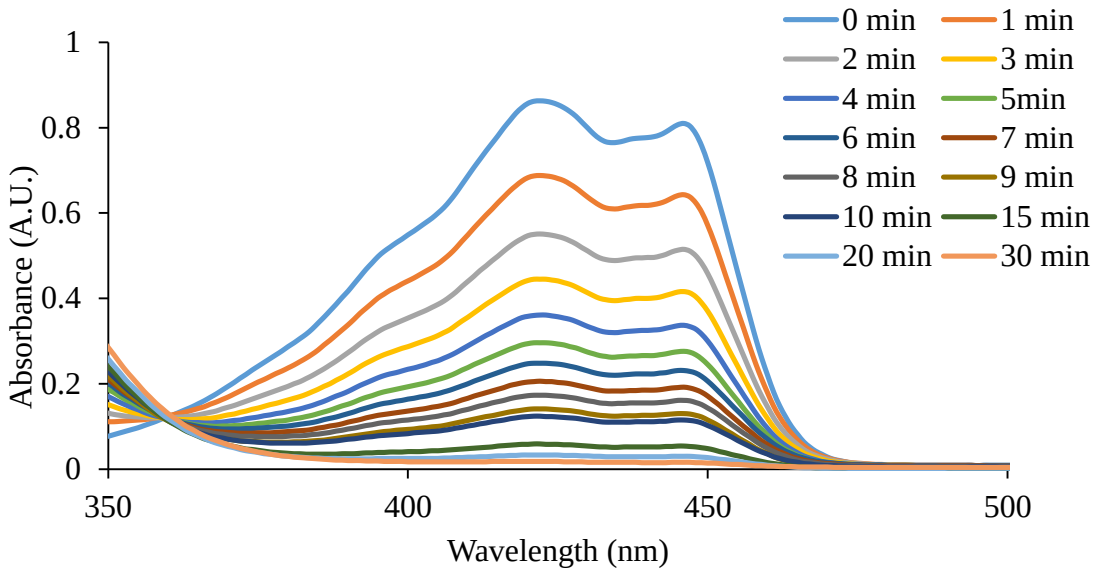


Figure 2.2 – Steady-state photolysis of **1a** in benzene using a 1 W 447 nm CW diode laser.

As the steady-state photolysis experiments were carried out in the absence of H-atom donors, electron donors, or oxygen and with relatively low intensity light, such

rapid and complete decomposition was not expected. To understand this result, computational modeling was carried out using Gaussian09.[87] Calculations on **1a**, its lowest triplet, its lowest quintet, and potential radical products were carried out using density functional theory (DFT) methods. Specifically, optimization and frequency calculations were carried out at the (U)M062x/6-311G+(d) level. Additionally, vertical excitation energies for excited singlets and triplets were determined using time-dependent density functional theory (TD-DFT) calculations from optimized S_0 and T_1 geometries, respectively. The results of these calculations can be seen in Table 2.1. Calculations were also performed on possible radical products and, from the calculations, approximate bond dissociation energies (BDEs) were calculated (Scheme 2.4). It appears that the cleavage of the central C-C bond via the Norrish type I reaction (Scheme 2.4, pathway A) is the lowest in energy.

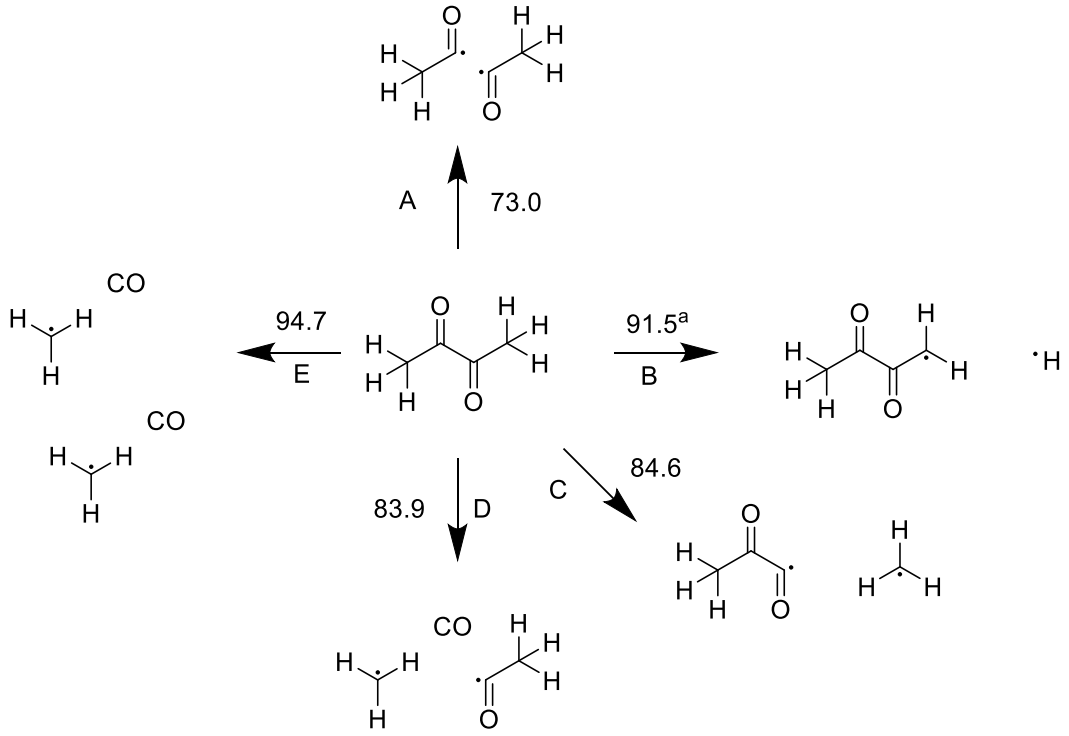
Table 2.1 – Vertical excitation energies for **1a**.

State	Energy[a] (kcal/mol)	State	Energy[b] (kcal/mol)	Excitation Wavelength[d] (nm)	State	Energy (kcal/mol)
S_0	0					
S_1	62.8	T_1	56.0[c]		Q_1	157.1[c]
S_2	104.1	T_2	85.3	975.68		
S_3	153.3	T_3	104.8	586.75		
S_4	163.2	T_4	130.6	383.33		
		T_5	139.6	342.34		
		T_6	159.3	276.96		
		T_7	160.2	274.56		
		T_8	160.7	273.24		
		T_9	169.6	251.86		
		T_{10}	179.4	231.72		
		T_{11}	183.1	224.97		
		T_{12}	185.5	220.92		
		T_{13}	188.4	215.99		

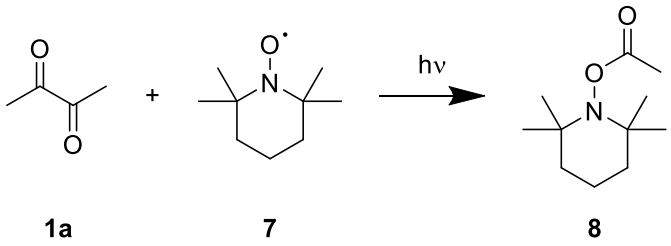
[a]vertical energies at S_0 geometry [b]vertical energies at T_1 geometry [c]adiabatic energy relative to S_0 [d]$T_1 \rightarrow T_n$

Radical trapping experiments were performed with (2,2,6,6-tetramethylpiperidin-1-yl)oxyl (TEMPO, **7**) to determine if acyl radicals were formed from **1a** photolysis. If acyl radicals are a product of **1a** photolysis, in the presence of **7**, 2,2,6,6-tetramethylpiperidin-1-yl acetate, **8**, should be formed (Scheme 2.5). **8** was synthesized independently and used as a standard for comparison with photolysis products. Solutions of 139.2 mM **7** and 1.6 M **1a** in benzene were photolyzed with a 1 W 447 nm CW diode laser for various times and production of **8** was monitored via gas chromatography. After 1 h of photolysis 44.5 mM of **8** was detected indicating that acyl radicals were in fact a product of **1a** photolysis (See Chapter 5).

Scheme 2.4 – **1a** radical products with calculated BDEs (kcal/mol). [a]Carbon-centered radical possessed one imaginary frequency.



Scheme 2.5 – Radical trapping with TEMPO (**7**).



1a **7** **8**

The effect of triplet quenching on decomposition was determined using *E*-stilbene (E_T=49.2 kcal/mol) as a triplet quencher. Because *E*-stilbene has a lower triplet energy than **1a** (E_T=56.4 kcal/mol), adding it to the photolysis sample will suppress decomposition. A Stern-Volmer analysis of the decomposition with various amounts of quencher will determine if **1a** triplet is necessary for degradation. Solutions containing 0.8% v/v **1a** in benzene were photolyzed for five minutes with a 0.60 W 447 nm CW diode laser with increasing concentrations of *E*-stilbene. The decomposition of **1a** was measured using UV-Vis spectroscopy, specifically by monitoring the change in absorbance at 422 nm before and after photolysis.

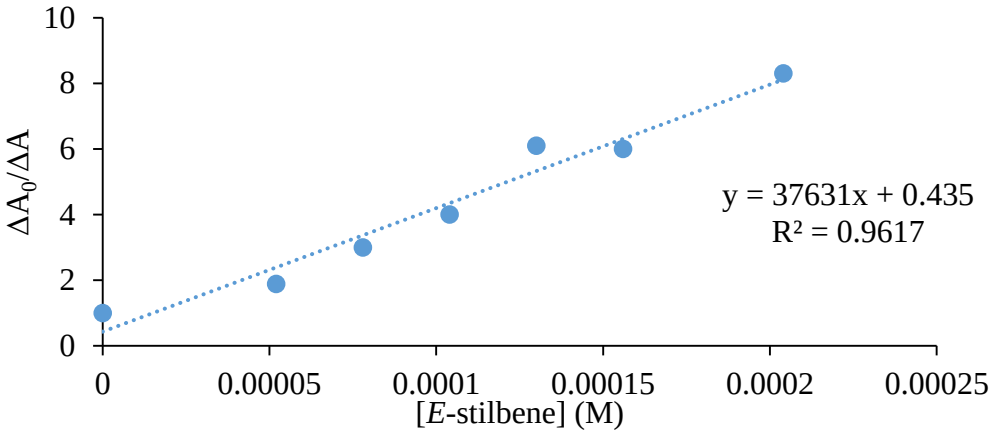


Figure 2.3 – Stern-Volmer plot of **1a** with *E*-stilbene – $k_Q = 2.6\times10^8\ M^{-1}$.

The ratio of the change in absorbance with each concentration of quencher to absorbance change in the absence of quencher ($\Delta A_0/\Delta A$) was plotted versus the

concentration of quencher (Figure 2.3) and a line of best fit was generated. Using Equation 2.1, the slope from the line of best fit, and a reported lifetime for triplet **1a** of 145 μs,[88] the quenching rate was determined to be 2.6×10^8 M^{-1}. The quenching of **1a** decomposition with *E*-stilbene indicates that the T_1 state of **1a** is a necessary intermediate in the decomposition pathway.

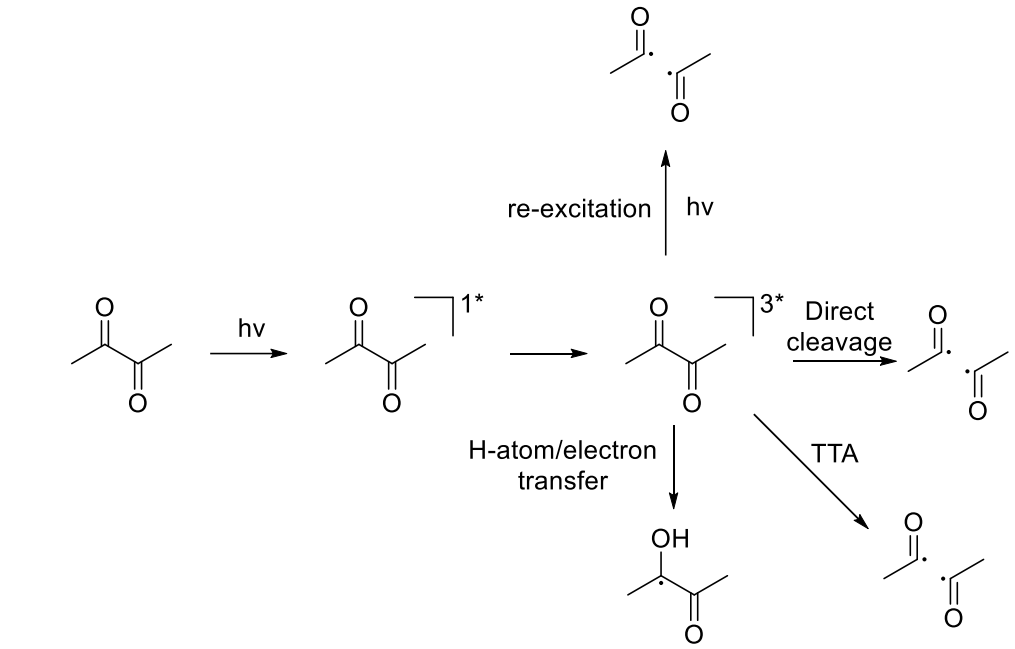
$$\frac{\Delta A_0}{\Delta A} = 1 + k_q\tau[Q] \qquad (Equation\ 2.1)$$

There are several potential pathways that could possibly explain the decomposition of **1a** in the absence of a co-initiator (Scheme 2.6). The quenching analysis reveals that **1a** forms a triplet but from that triplet there are many pathways that could lead to radicals. One possibility is that the triplet itself can dissociate to form radicals. Calculations show that the BDEs for radical formations are higher than the excited state energy of the triplet making this pathway unlikely. Another possibility would be formation of a ketyl radical through various H-atom or electron transfer processes. However, in an inert solvent such as benzene and in the absence of co-initiator, this pathway also seems unlikely. The two remaining pathways are re-excitation of the triplet and triplet-triplet annihilation.

Initially, it was believed that the observed decomposition was from a re-excitation pathway where triplet **1a** would be further excited by absorption of an additional photon. Such a re-excitation could yield an upper excited state with sufficient energy to induce a Norrish type I reaction. Table 2.1 shows that, from T_1, a 447 nm photon has sufficient energy to populate T_2 and T_3, each of which has energy necessary

to form radicals. Interestingly, nanosecond transient absorption spectroscopy of **1a** shows a negative ΔOD at 447 nm, the wavelength where re-excitation would

Scheme 2.6 – Possible radical formation pathways for **1a**.



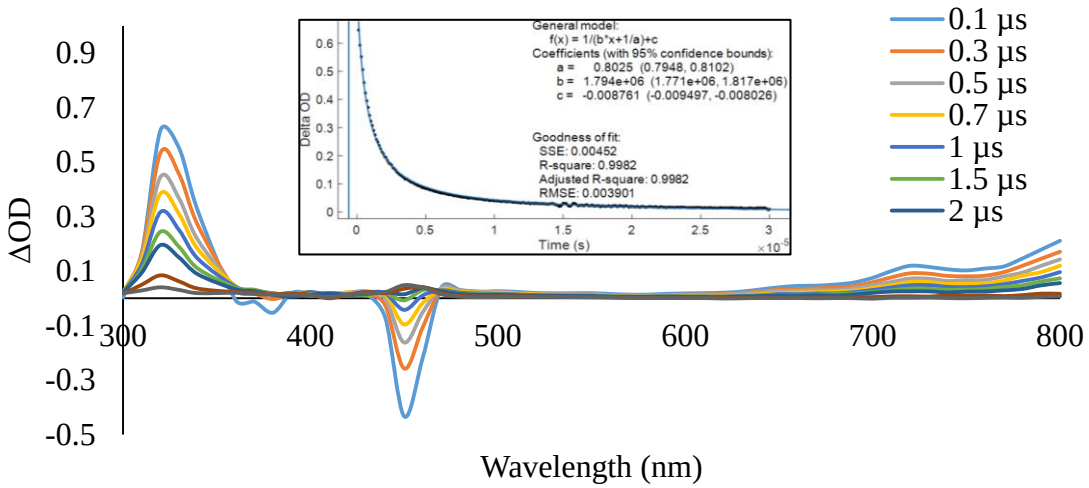


Figure 2.4 – Transient absorption spectrum of **1a** in benzene at various times following 355 nm pulsed excitation. The transient assigned to triplet **1a** has a large absorbance c. 320 nm. Around 650 nm, 720 nm, and 800 nm there appear to be vibronic bands. The large bleaching event at 450 nm indicates that triplet **1a** absorbs significantly less than the ground state. *Inset*: Waveform of triplet **1a** at 320 nm. Kinetic analysis of this waveform fits best with a second-order process. The second-order rate constant is 1.8×10^{6} $M^{-1}s^{-1}$ giving an excited state lifetime of 5.6×10^{-7} s.

occur (Figure 2.4). However, such a bleaching event in the transient spectrum does not necessarily rule out re-excitation. A negative ΔOD does not mean that triplet **1a** is transparent at 447 nm but rather that triplet **1a** absorbs less light at 447 nm than the ground state **1a**. Thus, re-excitation could still occur although unlikely due to ground state **1a** acting as an inner filter.

2.4 Investigation into the Mechanism

To determine if re-excitation was in fact occurring, several steady-state photolysis experiments were performed using various powers of a 447 nm laser. The results of these experiments can be seen in Figure 2.5. It was observed that higher laser powers led to faster decomposition. Interestingly, a photolysis threshold where decomposition ceased below a certain power was not observed. For re-excitation, a photolysis threshold would be expected where the power is sufficiently low so as to eliminate multiphoton processes. It is possible, however, that such low power was merely not reached by this experiment. Still, a re-excitation mechanism should be quadratic with respect to power, but further investigation revealed that there was a linear relationship between initial rate of decomposition and laser power (Figure 2.6).

Transient absorption spectroscopy combined with decomposition at relatively low intensities of light suggests that re-excitation is unlikely to be a major pathway. Additionally, the decay of triplet **1a** fits to a second-order decay rate rather than first-order (Figure 2.4, inset). Phosphorescence or non-radiative relaxation of the triplet would be unimolecular and therefore first-order. A second-order decay rate would be more consistent with a bimolecular reaction such as triplet-triplet annihilation. In a

TTA mechanism, two **1a** molecules in the excited triplet state collide propelling one **1a** molecule to a higher energy state and returning the other to the S_0 state (Scheme 2.7). If TTA is the main process for radical formation, TTA could also be the major pathway for triplet decay, consistent with a second-order decay rate.

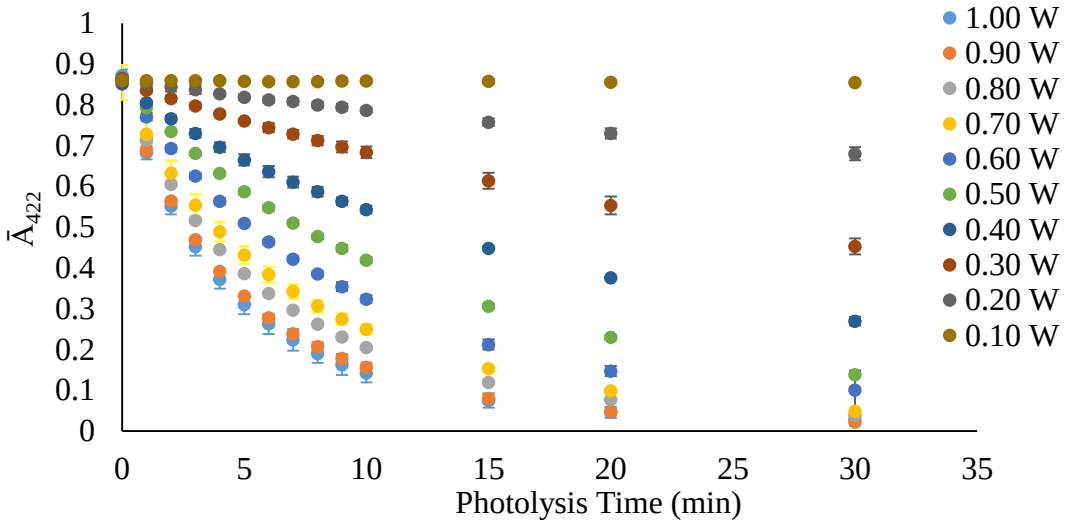


Figure 2.5 – Steady-state photolysis of **1a** in benzene using a 447 nm CW diode laser at various powers. Higher power outputs from the laser cause faster decomposition of the visible absorption band of **1a** (measured at 422 nm). $\bar{A}_{422}$ was calculated by taking the average absorption of three separate **1a** samples at 422 nm at the corresponding time point. Error bars represent the standard deviation of the three experiments.

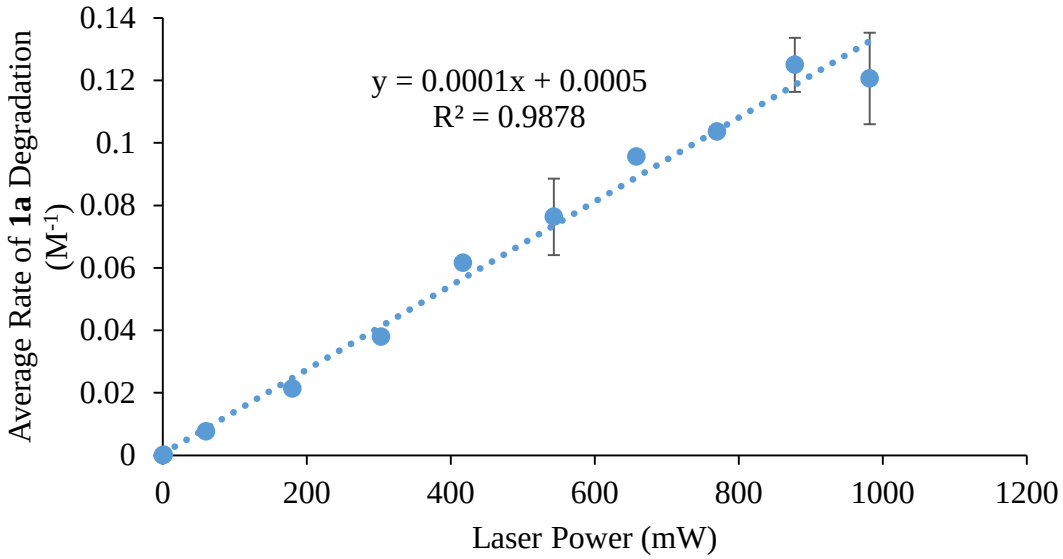
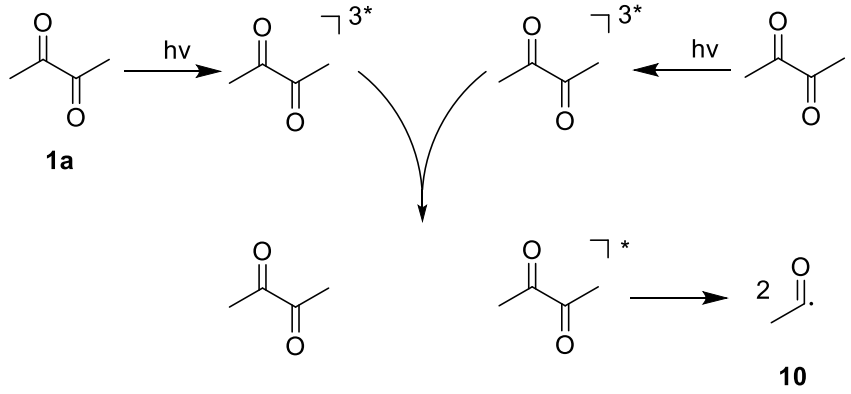


Figure 2.6 – Rate of **1a** decomposition is linear with respect to laser power.

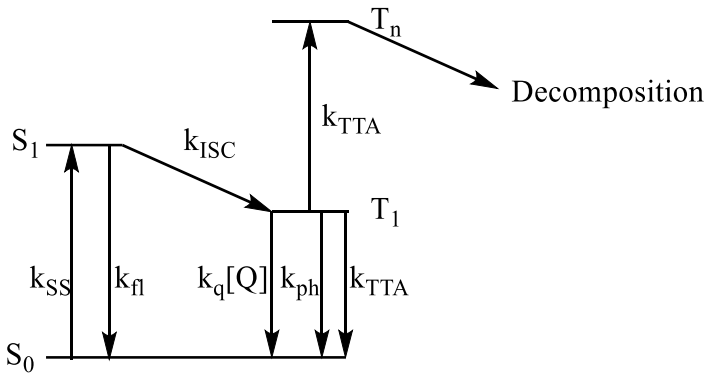
Scheme 2.7 – Triplet-triplet annihilation of **1a**. Annihilation consumes two excited triplet **1a** molecules and produces on ground state **1a** and one high energy excited **1a**. This high energy excited state is believed to be the source of acyl radicals (**10**).



The rate of **1a** decomposition is linear with respect to laser power indicating that the radical-forming reaction is likely a one photon process, inconsistent with a re-excitation mechanism. When the data are presented as a log-log plot, as seen in Figure 2.7, the slope represents the effective number of photons necessary for a reaction, one in the case of **1a**. Although this seems to be inconsistent with a triplet-triplet

annihilation pathway, a one photon process is regularly observed for triplet-triplet annihilation processes at high power densities.[85,86,89,90] This is explained by examining a kinetic model of the decomposition process (Scheme 2.8). In this model, ground state **1a** (S_0) is depleted by excitation to S_1 (k_{SS}) using a light source with power I and restored by fluorescence from S_1 (k_{fl}), quenching of T_1 with a quencher Q (k_q), phosphorescence from T_1 (k_{ph}), and TTA of two molecules in the T_1 state (k_{TTA}) (Equation 2.2). The S_1 state is populated by excitation of S0 and is depleted by fluorescence and intersystem crossing (k_{ISC}) to T_1 (Equation 2.3). The T_1 state is populated by intersystem crossing from S_1 and is depleted by phosphorescence, quenching, and TTA (Equation 2.4). Higher excited states (represented in Scheme 2.8 as T_n) are populated via TTA (Equation 2.5). Only these higher excited states lead to decomposition (Table 2.1, Scheme 2.4). Equations 2.6-2.8 come from applying the steady-state approximation to Equation 2.3. Applying the steady-state approximation to Equation 2.4 results in Equation 2.9. Equation 2.9 is simplified to Equation 2.10 by assuming $k_q << k_{TTA}$ and $k_{ph} << k_{TTA}$. These assumptions are based on the observation that the phosphorescence lifetime for **1a** in a solid matrix (where TTA is nearly completely eliminated) is 10.0 ms compared to a lifetime of 145 μs in solution.[91] Equation 2.10 can be rearranged to Equation 2.11. Applying Equation 2.8 to Equation 2.11 gives Equation 2.12. Using Equation 2.12 to solve Equation 2.5 gives Equation 2.13. Equation 2.13 shows that the rate of decomposition is directly proportional to power (I) which explains the one photon appearance of the log-log plot.

Scheme 2.8 – Kinetic model for **1a** triplet-triplet annihilation.



$$\frac{-dS_0}{dt} = k_{SS}I[S_0] - k_{fl}[S_1] - \left(k_{ph} + k_q[Q]\right)[T_1] - k_{TTA}[T_1]^2 \qquad (Equation\ 2.2)$$

$$\frac{dS_1}{dt} = k_{SS}I[S_0] - \left(k_{ISC} + k_{fl}\right)[S_1] \qquad (Equation\ 2.3)$$

$$\frac{dT_1}{dt} = k_{ISC}[S_1] - \left(k_{ph} + k_q[Q]\right)[T_1] - k_{TTA}[T_1]^2 \qquad (Equation\ 2.4)$$

$$\frac{dT_n}{dt} = k_{TTA}[T_1]^2 \qquad (Equation\ 2.5)$$

$$\frac{dS_1}{dt} = 0 = k_{SS}I[S_0] - \left(k_{ISC} + k_{fl}\right)[S_1]_{\,SS} \qquad (Equation\ 2.6)$$

$$k_{SS}I[S_0] = \left(k_{ISC} + k_{fl}\right)[S_1]_{\,SS} \qquad (Equation\ 2.7)$$

$$[S_1]_{\,SS} = \frac{k_{SS}I[S_0]}{k_{ISC} + k_{fl}} \qquad (Equation\ 2.8)$$

$$\frac{dT_1}{dt} = 0 = k_{ISC}[S_1]_{SS} - \left(k_{ph} + k_q[Q]\right)[T_1]_{SS} - k_{TTA}[T_1]_{SS}^2 \qquad (Equation\ 2.9)$$

$$\frac{dT_1}{dt} = 0 = k_{ISC}[S_1]_{SS} - k_{TTA}[T_1]_{SS}^2 \qquad (Equation\ 2.10)$$

$$k_{TTA}[T_1]_{SS}^2 = k_{ISC}[S_1]_{SS} \qquad (Equation\ 2.11)$$

$$k_{TTA}[T_1]_{SS}^2 = \frac{k_{ISC}k_{SS}I[S_0]}{k_{ISC} + k_{fl}} \qquad (Equation\ 2.12)$$

$$\frac{dT_n}{dt} = \frac{k_{ISC}k_{SS}I[S_0]}{k_{ISC} + k_{fl}} \qquad (Equation\ 2.13)$$

A Stern-Volmer analysis was performed with biphenyl (E_T=65.5 kcal/mol) to determine if it was possible to quench the T_2, or higher, state of **1a** (E_{T2}=85.3 kcal/mol, Table 2.1). No appreciable quenching was observed. A lack of quenching with biphenyl does not rule out higher excited states accessed via T_1, however.

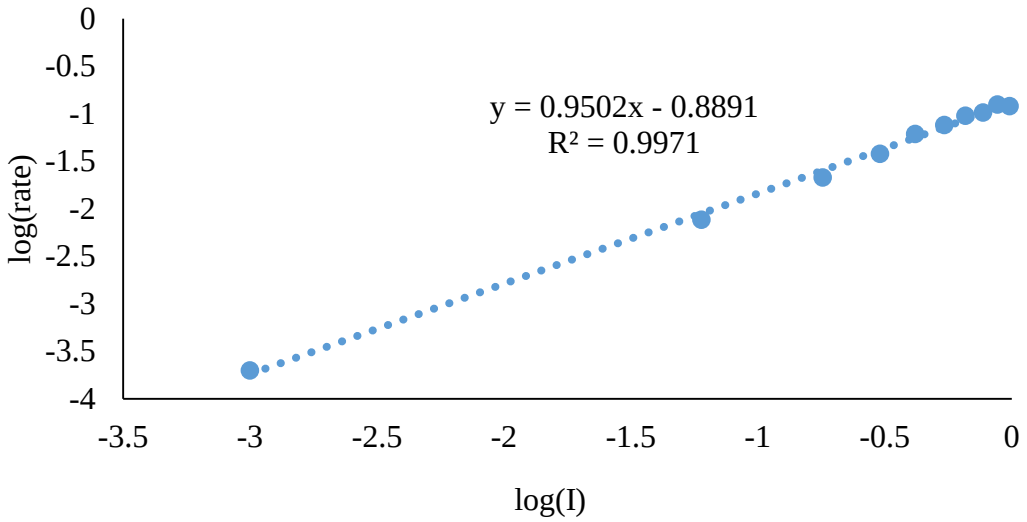


Figure 2.7 – A log-log plot of rate of **1a** decomposition and laser power.

Laser flash photolysis experiments were performed on solutions of **1a** in *cis*-decalin at various temperatures. The viscosity of *cis*-decalin is highly temperature dependent: at higher temperatures it is less viscous and at lower temperatures it is more

viscous (Table 2.2). TTA requires diffusion, but re-excitation would be independent of both diffusion and temperature. Thus, by varying the temperature (and therefore viscosity) of the samples, the diffusion dependence of the triplet lifetime can be determined. Waveforms of the **1a** triplet were measured at several different temperatures revealing that lowering the temperature of the sample increases the triplet lifetime and raising the temperature decreases the triplet lifetime (Figure 2.8, Table 2.2). This is consistent with a TTA pathway: as temperature is lowered, diffusion becomes slower resulting in more persistent transient signals.

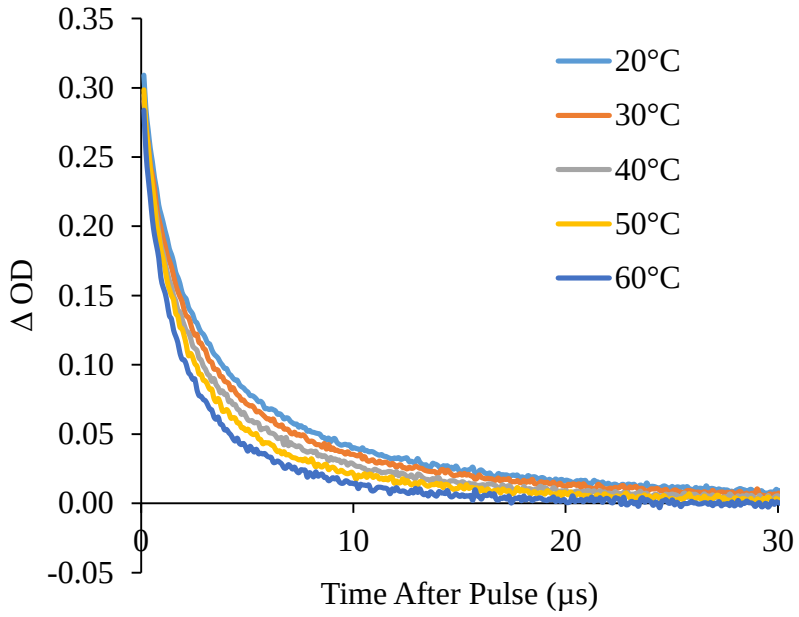


Figure 2.8 – Waveforms of 5% w/v **1a** in *cis*-decalin measured at 330 nm. Excitation at 266 nm. Lifetimes decrease at higher temperatures due to lower viscosity of solvent. Samples purged with nitrogen before use. Provided by Matthew Thum.

Table 2.2 – Temperature and viscosity dependence of **1a** triplet decay rate constant. The sample consisted of **1a** in *cis*-decalin and was purged with nitrogen before use. According to the Stokes-Einstein equation, the term T/ η is directly proportional to the diffusion constant, D, of the solution (Equation 2.14). Provided by Matthew Thum.

Temperature, T (K)	Viscosity, η (mPa*s)	T/η (K/mPa*s)	Rate Constant ($M^{-1}s^{-1}$)	Error ($M^{-1}s^{-1}$)
293	3.0	98	8.00×10^{9}	$\pm9.50\times10^{7}$
303	2.29	132	8.00×10^{9}	$\pm8.20\times10^{7}$
313	1.88	166	8.60×10^{9}	$\pm1.59\times10^{8}$
323	1.63	198	1.00×10^{10}	$\pm2.20\times10^{8}$
333	1.46	228	1.25×10^{10}	$\pm2.80\times10^{8}$

$$D = \frac{k_B T}{6\pi r \eta} \qquad (Equation\ 2.14)$$

*2.5 Polymerization with **1a***

To determine if **1a** could be used as a photoinitator, monomer mixtures of 5:1 divinylbenzene:**1a** were exposed to different levels of irradiation under various conditions (Table 2.3). Divinylbenzene was chosen as a monomer because it creates crosslinked polymers in the presence of radicals. The crosslinked polymers can be easily observed by eye allowing for quick detection of polymerization. Before preparing the monomer mixture, divinylbenzene was extracted with a saturated aqueous solution of sodium bicarbonate to remove the phenolic inhibitor. The samples described by entries 1-7 were placed in septum-sealed vials and purged with the respective gas for 30 minutes prior to photolysis. The samples described in entries 8-10 were not purged and the vials were closed with screw on caps.

The first experiment show that the monomer mixture can be polymerized with a 1.08 W 447 nm CW diode laser (entry 1). Additionally, when the beam is defocused so that the photons are more widely distributed throughout the sample, polymerization can still occur (entry 2). Reducing the power of the defocused beam and increasing photolysis time also yields polymer (entry 3). Although the experiment described in entry 3 shows that polymerization can occur with low intensity irradiation and a large exposure area, room light alone is not sufficient to cause polymerization (entry 4). Additionally, the monomer mixture is stable long-term in the absence of light (entry 5). Purging samples with oxygen before photolysis does not preclude polymerization (entry 6, 7). This apparent oxygen tolerance may be due to limited solubility of oxygen in the monomer or TTA outcompeting oxygen quenching. A less intense light source did not cause polymerization (entry 8). Entry 9 describes a sample of monomer mixture that does not contain **1a**. After photolysis, no polymerization was observed showing the necessity of **1a**. Once the photoinitator is added and irradiation resumes, polymerization of the monomer mixture occurs (entry 10).

Table 2.3 – Polymerization data for 5:1 divinylbenzene:**1a** mixtures.

Entry	Light Source	Atmosphere	Power	Time	Polymer
1	447 nm Laser	N_2	1.08 W	1 h	Yes
2	447 nm Laser[a]	N_2	1.08 W	1 h	Yes
3	447 nm Laser[a]	N_2	0.27 W	3 h	Yes
4	Room Light	N_2	-	>3 d	No
5	Dark	N_2	-	>10 d	No
6	447 nm Laser[a]	O_2	0.27 W	3 h	Yes
7	447 nm Laser	O_2	1.08 W	1 h	Yes
8	Rayonet (419 nm)	Air	-	1 h	No[b]
9[c]	447 nm Laser	Air	1.08 W	1 h	No
10[d]	447 nm laser	Air	1.08 W	1 h	Yes

[a]Laser beam defocused. [b]Formed polymer after several days while kept in the dark. [c]No **1a**. [d]**1a** added to the sample from entry 9 and photolyzed for an additional 1 h.

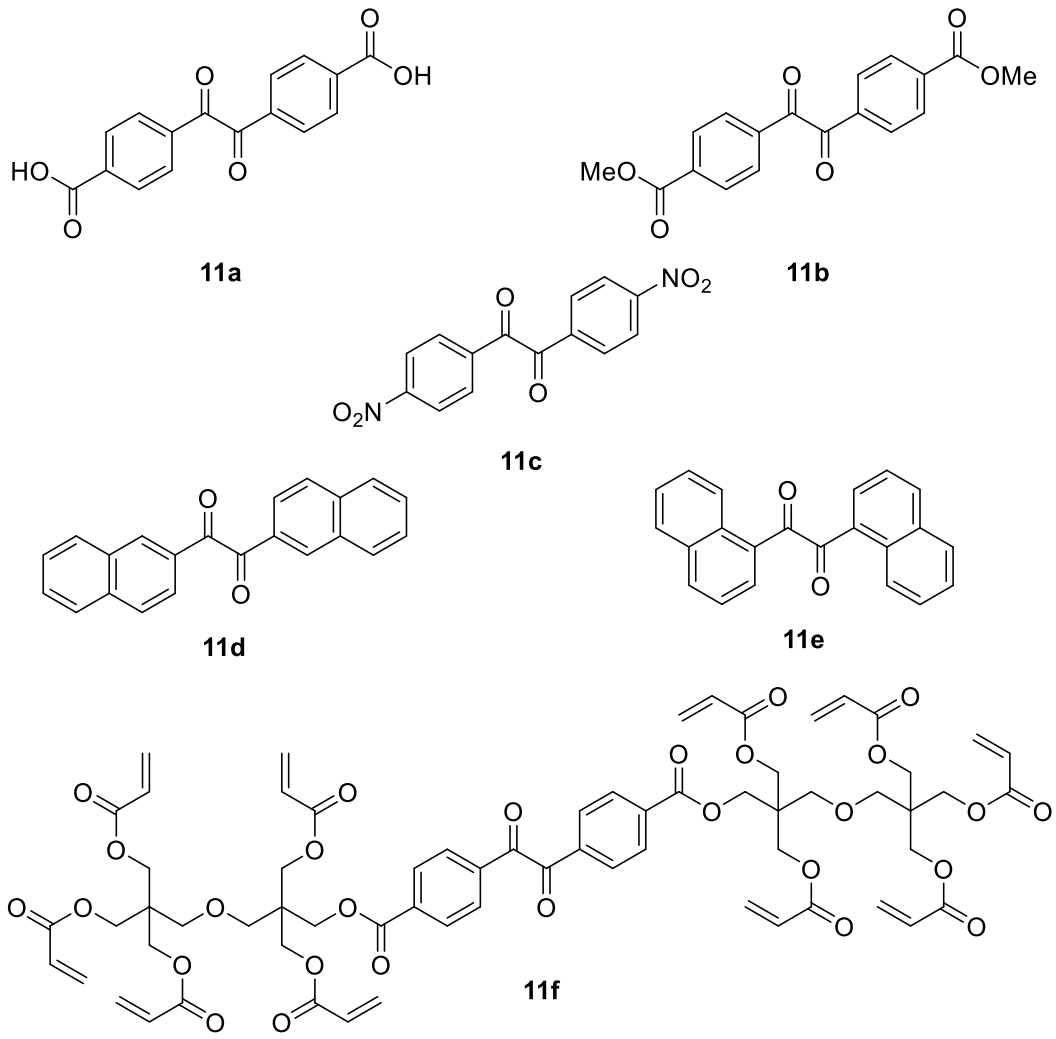
2.6 Conclusions

Radical formation via triplet-triplet annihilation of excited **1a** is supported by steady-state photolysis, Stern-Volmer analysis, and laser flash photolysis. Additionally, a TTA pathway is consistent with product analysis, computational modeling, and polymerization data. These data, along with the reduced absorbance at 447 nm observed in the transient absorption spectrum of **1a**, indicate that triplet-triplet annihilation is the major pathway to radical formation but do not rule out the possibility of a re-excitation pathway. To use **1a** for multicolor systems, TTA would have to be limited. This may be achievable using viscous monomer mixtures to limit diffusion. Another possibility is using a bulkier α-diketone, such as the compounds shown in

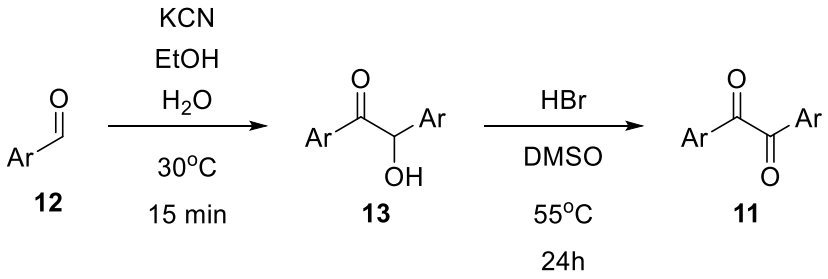
Scheme 2.9. These α-diketones can be synthesized from aryl aldehydes by performing a cyanide catalyzed benzoin condensation followed by oxidation to give (Scheme 2.10).[92] Multi-acrylate α-diketone **11f** is of particular interest for lithography, not only due to its size, but also because it can act as a cross-linker for radical polymerization.

Compound **11f** was synthesized according to the procedure shown in Scheme 2.11. First, Fisher esterification was performed with 4-formylbenzoic acid, **12a**, and methanol to yield methyl 4-formylbenzoate, **12b**.[93] Compound **12b** was treated with potassium cyanide in water and ethanol to give the corresponding benzoin, **13b**. Oxidation of **13b** with hydrobromic acid yielded α-diketone **11b**. Hydrolysis of diester **11b** gave dicarboxylic acid **11a**. Compound **11a** was treated with sequentially with thionyl chloride then dipentaerythritol and finally acryloyl chloride to give **11f** as an orange solid. Crude compound **11f** was given to collaborators for polymerization experiments. ^{1}H-NMR of **11f** can be found in Chapter 5.

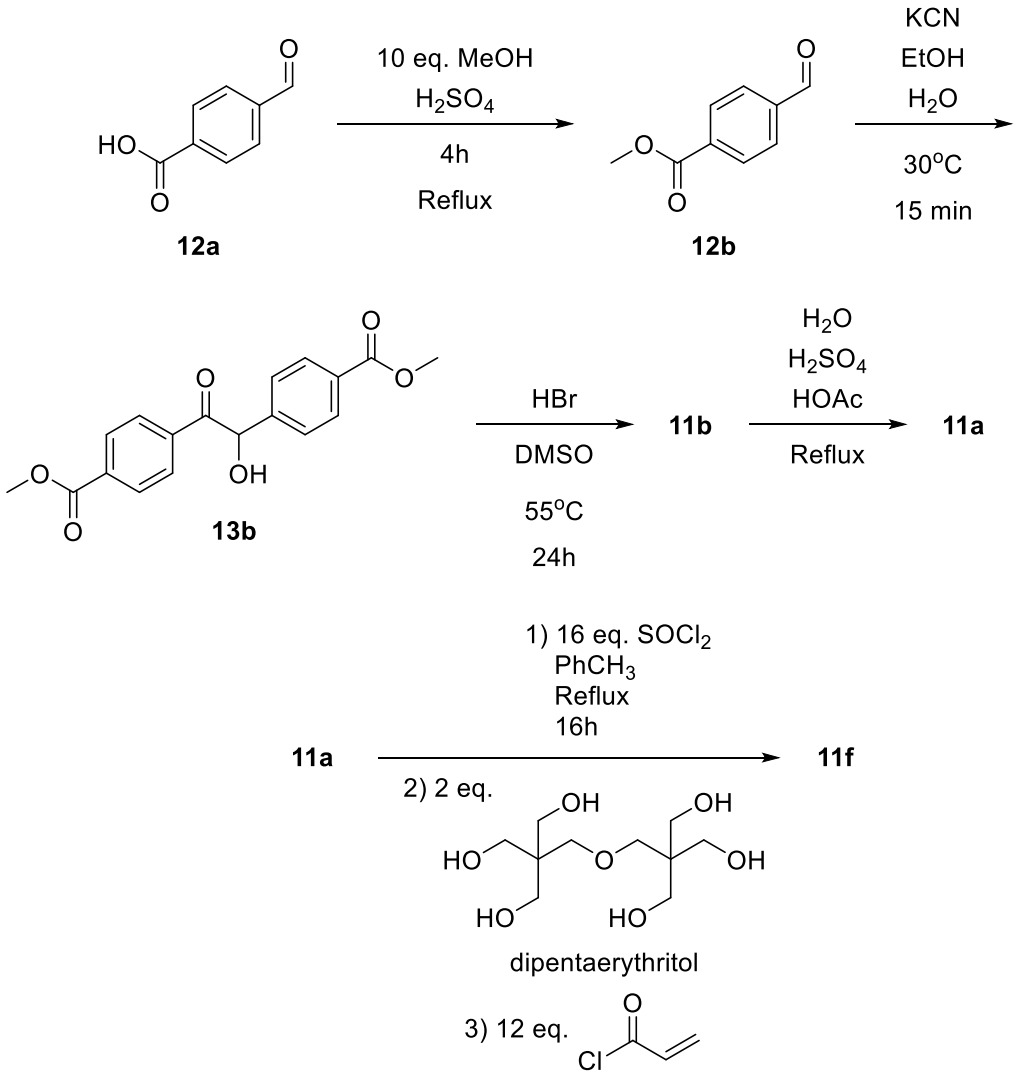
Scheme 2.9 – Bulky α-diketones.



Scheme 2.10 – Synthesis of aryl α-diketones.



Scheme 2.11 – Synthesis of α-diketone **11e**.

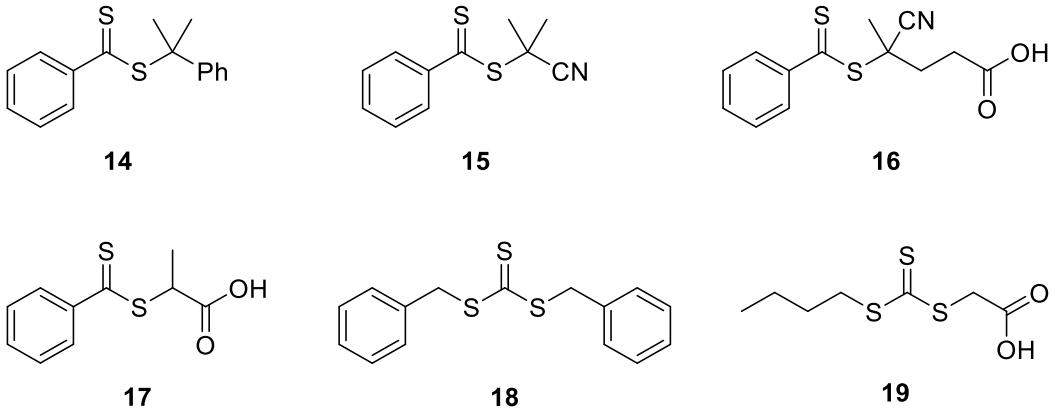


Chapter 3: Photophysics of Dithioesters and Trithiocarbonates

3.1 Introduction

Reversible addition-fragmentation chain transfer (RAFT) is a popular polymerization technique used to control polymer growth and create well-defined polymers. The key to RAFT is the use of dithioesters and trithiocarbonates as chain transfer agents known as iniferters (Scheme 3.1).[94–97] The iniferter plays three important roles; it is the INItiator, acts as a transFER agent, and TERminates the growing radical. In the twenty years since its invention, RAFT has been used for a variety of applications including the synthesis of copolymers,[98] supramolecular chemistry,[99] surface modification,[100] and optoelectronics.[101]

Scheme 3.1 – Common RAFT agents.[94,97,102–104]



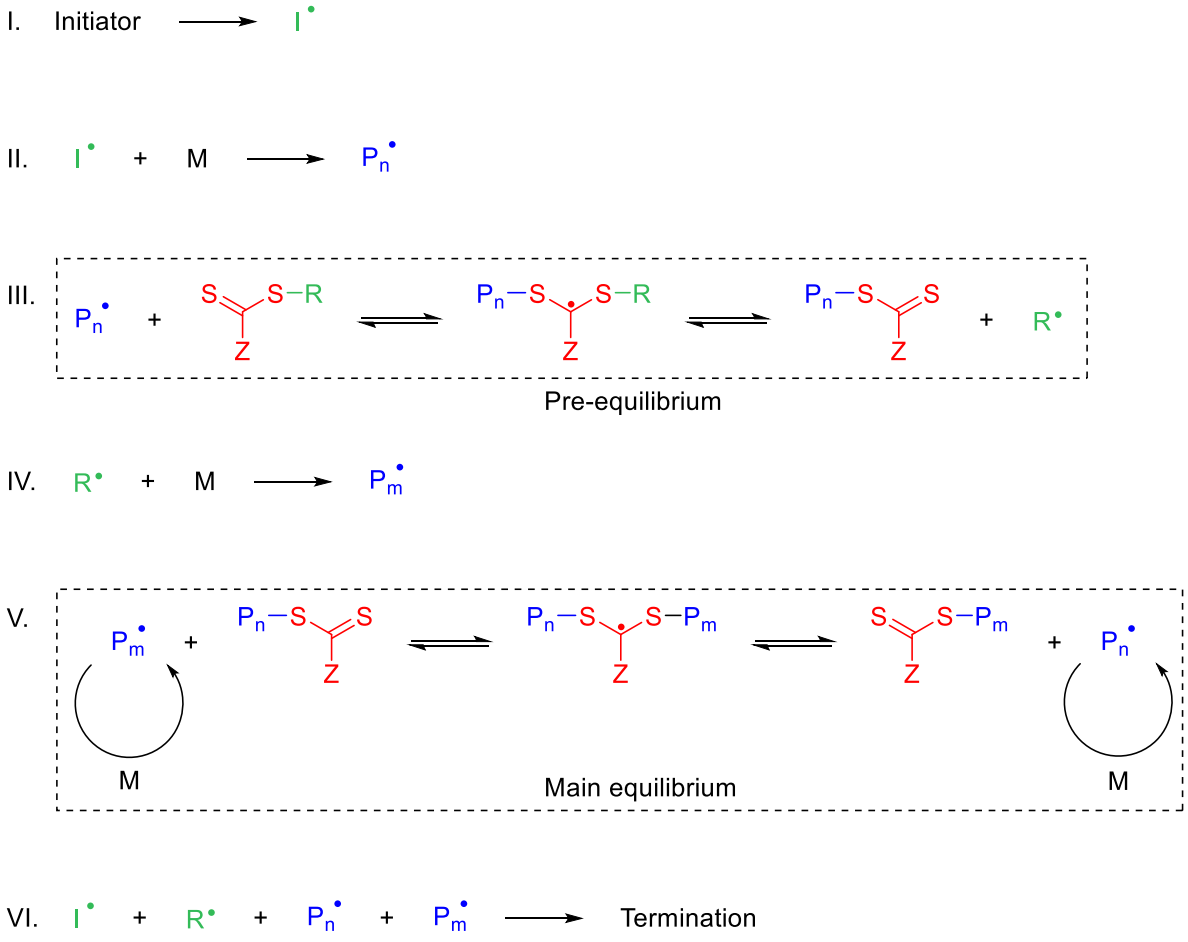
A general mechanism for RAFT polymerization can be seen in Scheme 3.2. The first step is the generation of radicals from an initiator (I). Radicals can be generated in variety of ways including thermal decomposition of commercially available compounds or direct irradiation of the RAFT agent itself.[94,105] Once formed, the

radicals add to monomers to initiate polymerization (II). The next step (III) is known as the pre-equilibrium where the growing polymer chain adds reversibly to the RAFT agent and becomes dormant. The resulting carbon-centered radical can then eliminate its side chain to form additional radicals for initiation (IV). Once polymerization is fully underway, the main equilibrium of the RAFT process begins (V). In this equilibrium growing polymer chains are predominantly capped by the iniferter but are able to return to their active form where monomer addition is possible. This step is key to the well-controlled polymerizations observed with RAFT as it greatly reduces termination reactions (VI) that lead to uncontrolled polymerization.

Current photoactivation of the RAFT process centers on the use of photoinitiators for radical generation, photoredox catalysts for photoinduced electron-transfer (PET) RAFT, or direct photo-RAFT.[103] Photoinitiation RAFT replaces the more common thermal radical initiators for a photochemical radical generator. Photoinitiation RAFT can use type-I initiators (Scheme 3.3A) or type-II initiators (Scheme 3.3B).[103,106,107] Type-I initiators are unimolecular photoinitiators that generate radicals upon irradiation. Type-II initiators use a co-initiator (often an amine) to generate radicals. Upon excitation, the type-II initiator enters an excited state. This excited state undergoes a bimolecular reaction with the co-initiator to generate radicals and initiate polymerization. Cai and coworkers in particular have used type-I initiators extensively. Using photoinitiators such as diphenyl(2,4,6-trimethylbenzoyl)phosphine oxide (**22**) and sodium phenyl(2,4,6-trimethylbenzoyl)phosphinate (**23**), Cai et al. have polymerized a variety on monomers in a wide range of condition using a broad range

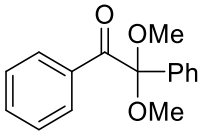
of wavelengths (including sunlight) to make diverse structures such as block copolymers, vesicles, and nanostructured polyionic complexes.[108–115]

Scheme 3.2 – General mechanism for reversible addition-fragmentation chain transfer polymerization with a dithioester.[97]



Scheme 3.3 – Unimolecular type-I (A) photoinitiators and bimolecular type-II (B) photoinitiators.

A) Type-I Photoinitiators



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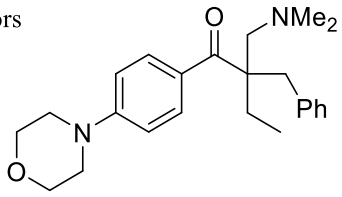

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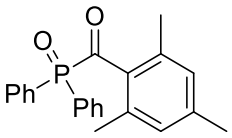

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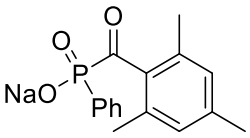

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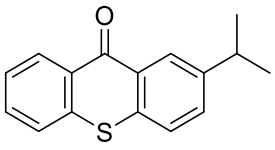
B) Type-II Photoinitiators



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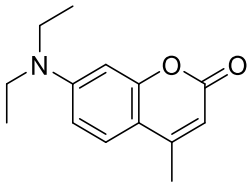

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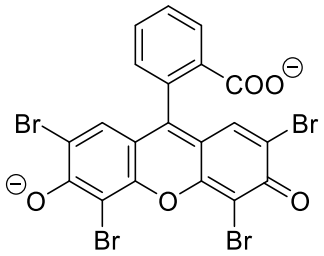

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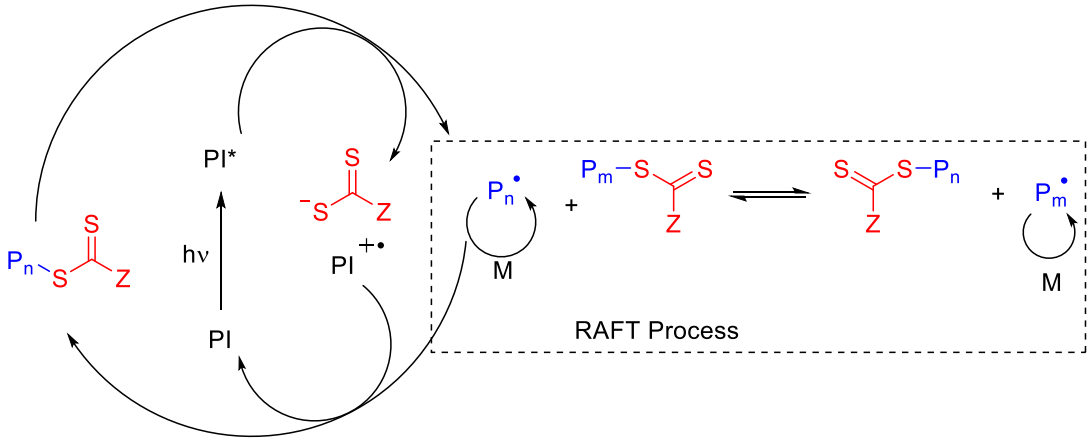
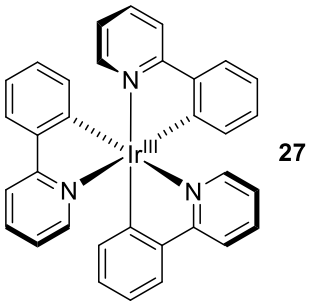
PET-RAFT uses a photoinitiator (PI) to transfer an electron to the RAFT agent generating the PI radical cation and a RAFT radical anion (not shown). The radical anion eliminates its sidechain to produce the propagating radical ($P_n^{\bullet}$) and the thiocarbonylthio anion. The propagating radical adds to monomers, increasing its length. The propagating radical can also add to the thiocarbonylthio anion and, coupled with an electron transfer to regenerate the photocatalyst (Scheme 3.4). Boyer et al. use a variety of photoinitiators to initiate RAFT polymerization. Using photoinitiators ranging from photoredox catalysts such as $Ir(ppy)_3$, **27**,[116–118] to organic dyes **29**-**31**[119–121] to chlorophyll *a*, **32**,[122–124] Boyer and co-workers have also demonstrated the ability to utilize near-IR wavelengths using pthalocyanine compound **28**[125] and bacteriochlorophyll *a*, **33**.[126] Using PET-RAFT, Boyer et al. polymerize a variety of monomers such as styrenes, acrylates, methacrylates, acrylamides, vinyl esters, vinyl phosponates, and *N*-vinylpyrrolidone and *N*-vinylcarbazole.

Scheme 3.4 – General mechanism for PET-RAFT and common photocatalysts.





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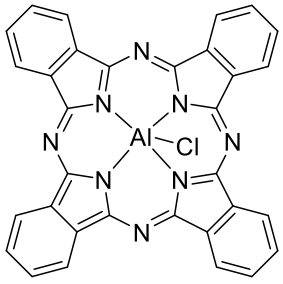

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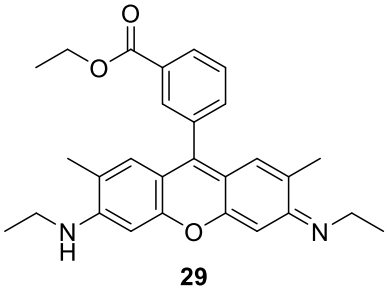

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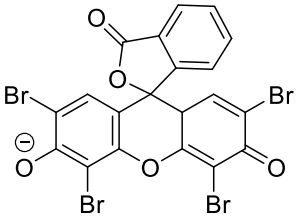

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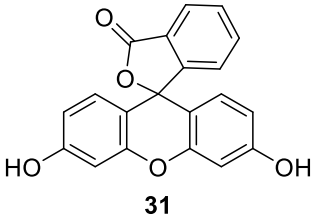

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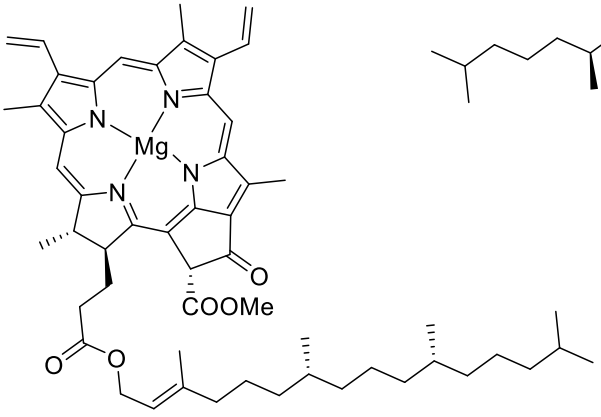

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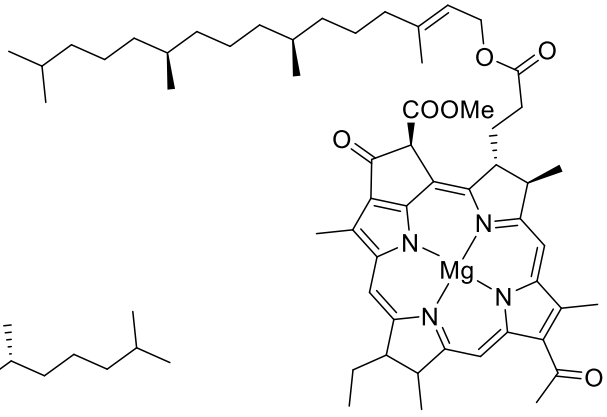


33

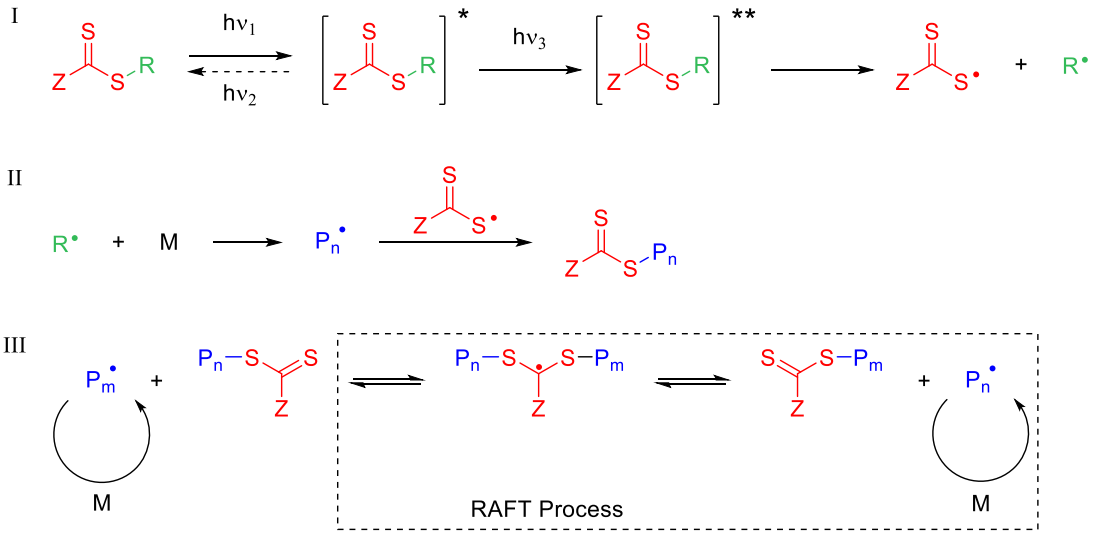
While the use of photoinitiators has provided polymer chemists with a variety of options for initiation of RAFT polymerization, there are some complications. The irradiation of the photocatalyst competes with simultaneous activation of the thiocarbonylthio chromophore of the RAFT agents leading to loss of control and degradation of dormant chains.[97,107] In PET-RAFT, the photoinduced electron transfer competes with energy transfer from the excited photocatalyst to the RAFT agent, leading again to loss of control and degradation.[125] This chapter will the direct photo-RAFT process where the RAFT agent is used as the photoinitiator (Scheme 3.5).

Step I of the RAFT polymerization can be replaced by direct photolysis of the RAFT agent to form radicals, a process known as photo-RAFT. This chapter will explore the potential of a multicolor photo-RAFT process. A hypothetical mechanism can be seen in Scheme 3.5. The first step in the multicolor photo-RAFT process would be irradiation of the RAFT agent and formation of a low energy excited state. This state should be low enough in energy that radical formation is not achievable and thermal relaxation to the ground state is the main process out of the excited state. Preferably, this state could also return to the ground state via irradiation with a different wavelength of light. Alternatively, a third wavelength could be used to generate a higher energy excited state that does lead to radical generation. The radical products formed are expected to be a carbon-centered radical and a sulfur-centered radical based on computational results (vide infra). The carbon-centered radical can initiate polymerization and the sulfur-centered radical would cap the growing polymer chain

(step II). Addition of an additional radical chain to the dormant RAFT-polymer adduct would lead to the main RAFT equilibrium.

As a multicolor approach will require excitation of the RAFT agent with multiple wavelengths of light, the excited sates of various RAFT agents and model compounds were investigated using computational methods. Additionally, the total energy of the various radical products formed from these iniferters was determined and the bond dissociation energies (BDEs) associated with their formation were calculated as well.

Scheme 3.5 – Proposed mechanism for multicolor photo-RAFT polymerization with a dithioester.



3.2 Benchmarking Results

To determine if a RAFT agent has potential for a multicolor photo-RAFT system, calculations were performed on various dithioesters and trithiocarbonates and their potential radicals products using density functional theory (DFT). The intent of these calculations is to determine the bond dissociation energies (BDEs) of S-X bonds in the iniferter to identify the radical products most likely to be formed by an excited

state bond homolysis. Additional time-dependent DFT (TD-DFT) calculations were performed on the RAFT agents to determine vertical transition energies corresponding to various higher excited states. From the results of these calculations it was determined which excited states have sufficient energy to effect bond cleavages and whether or not the excited state can be populated via two photon excitation.

Calculations on dithio- and trithio-compounds can be challenging due to the difficulty associated with estimating the stability of sulfur-centered radicals, both computationally and experimentally.[127,128] Fortunately, Coote and co-workers have established a procedure for benchmarking calculated BDEs using high level *ab initio* calculations with an additional correction for polar effects. Coote's calculations are in good agreement with experimental values but require significant computing time and do not address which excited states could lead to the radical formation.[127]

In an attempt to match the accuracy of Coote's results with less intensive methods, calculations on sulfur containing compounds and their corresponding radicals were carried out using DFT methods. A variety of methods were used to determine the energy of each compound, the corresponding sulfur-centered radical, and either the carbon-centered radical or a hydrogen atom. Although several different methods were applied, each calculation used the 6-311G++(d,p) basis set. The reported energies include the zero-point energy. The calculated bond dissociation energies were determined by finding the difference between the combined energy of the two radicals and the energy of the model compound. The calculated BDEs were then compared to experimental BDEs for each fragmentation. The calculated BDEs and the experimental

BDEs can be found in Table 3.1. BDEs determined at the (U)MN12SX/6-311G++(d,p) level showed the best agreement with the known values.

Table 3.1 – Benchmarking DFT methods for determining bond dissociation energies of S-X bonds.

Compound	Experimental (kcal/mol)[a]	CAM-B3LYP (kcal/mol)	B3LYP (kcal/mol)	MN12SX (kcal/mol)	PBE0 (kcal/mol)
H_3CS-CH_3	73.6 ± 0.8	64.73	63.30	72.07	69.70
PhS-CH_3	66.5 ± 2.5	57.75	55.26	64.84	62.33
CH_3CH_2S-$C(O)CH_3$	76.2 ± 2	60.98	59.86	69.57	67.12
CH_3S-CH_2Ph	61.4 ± 2	28.78	49.37	59.09	55.57
HS-H	91.2	86.80	86.87	90.14	87.36

[a]Experimental values come from Luo's Handbook of Bond Dissociation Energies in Organic Compounds.[129]

Additional calculations were performed to determine if geometries calculated with a smaller basis set could give similar results if single point frequency calculations used the same or larger basis sets. To do this, the geometries of the model compounds from Table 3.1 were optimized at the (U)MN12SX/6-31G(d) level. After optimization, single point frequency calculations were performed. The geometries and energies of the relevant radicals were calculated in the same fashion. All energies calculated this way include enthalpies. The calculated bond dissociation energies were determined by finding the difference between the combined energy of the two radicals and the energy of the model compound. The calculated BDEs and the experimental BDEs can be found in Table 3.2. It was determined that (U)MN12SX/6-311G++(d,p)//(U)MN12SX/6-31G(d) gave comparable results to both the BDEs calculated at the (U)MN12SX/6-311G++(d,p) level and the experimental results.

Table 3.2 – Benchmarking MN12SX functionals for S-X bond dissociation energies.

Compound	Experimental (kcal/mol) [a]	MN12SX/6-311++G(d,p) (kcal/mol)	MN12SX/6-311++G(2df,2p)//(U)MN12SX/6-31G(d) (kcal/mol)	MN12SX/6-311++G(d,p)//(U)MN12SX/6-31G(d) (kcal/mol)
H_3CS-CH_3	73.6 ± 0.8	73.55	73.65	73.57
PhS-CH_3	66.5 ± 2.5	66.19	74.21	64.87
CH_3CH_2S-$C(O)CH_3$	76.2 ± 2	70.35	72.17	70.85
CH_3S-CH_2Ph	61.4 ± 2	59.53	59.17	59.57
HS-H	91.2	91.31	91.13	91.27

[a]Experimental values come from Luo's Handbook of Bond Dissociation Energies in Organic Compounds.[129]

The (U)MN12SX/6-311G++(d,p)//(U)MN12SX/6-31G(d) method was compared to Coote's method and experimental BDEs for numerous S-H, S-C, S-S, and S-Cl bonds (Table 3.3). The MN12SX method is in good agreement with both the values determined experimentally and calculated using G3(MP2)-RAD for most of the molecules studied. One interesting exception is dithiobenzoic acid, the molecule shown in entry 6. Both computational methods underestimate the bond dissociation energy by more than 10 kcal/mol. However, when the predicted BDEs are plotted verses the empirically determined BDEs there appears to be good agreement (mean average deviation is 3.6 kcal/mol) and the point corresponding to entry 6 is one of the few outliers (Figure 3.1). Because the MN12SX method appears to be in good agreement

with other methods, it was used for subsequent calculations using RAFT agents and model compounds.

Table 3.3 – BDEs calculated using MN12SX, high level methods,[127] and experimentally determined.[130] Energies in kcal/mol. Complete results and additional information about the computational methods used can be found in Chapter 5 – Supplemental Information.

Entry	Compound	Experimental	G3(MP2)-RAD	(U)MN12SX/6-311G++(d,p)// (U)MN12SX/6-31G(d)
1	HS-H	91.10±0.01	90.7	91.3
2	CH3S-H	87.4±0.5	86.4	86.2
3	CH3CH2S-H	87.3	86.1	85.6
4	(CH3)2CHS-H	88.4±2	87.5	87.1
5	(CH3)3CS-H	86.6±2.2	87.7	87.3
6	C6H5C(S)S-H	87.9	75.6	73.3
7	CH3C(O)S-H	87	88	87
8	C6H5CH2S-H	86.9	88.6	86.1
9	C6H5S-H	83.5±1.1	80.2	77.8
10	*p*Cl-C6H4S-H	79.2	79.9	77.2
11	*p*CH3-C6H4S-H	78.3	79.3	76.8
12	*p*CH3O-C6H4S-H	76.9	77.8	75.3
13	*p*NO2-C6H4S-H	81.4	82.9	83.3
14	*p*NH2-C6H4S-H	69.8	76.9	73.5
15	HS-CH3	74.7±1	73.1	75.6
16	CH3S-CH3	73.6±0.8	71	73.6
17	CH3CH2S-CH3	73.4±1.5	71.5	72.9
18	HSS-CH3	57±1.5	61.1	56.5
19	CH3SS-CH3	57.4±1.5	58	59.3
20	C6H5S-CH3	66.5±2.5	66.3	64.9
21	HS-SH	64.7±1	62.2	61.3
22	CH3S-SCH3	65.2±0.9	63	59.8
23	CH3CH2S-SCH2CH3	66.1	64.4	58.9
24	HSS-SSH	33.6±2	41.6	36.5
25	CH3SS-SSCH3	32.9	37.4	32.7
26	C6H5S-SC6H5	51.2±3	52.8	44.5
27	CH3-Cl	70±3	65.4	62.9
28	CH3SS-Cl	51±2.5	53.5	50.2
29	C6H5S-Cl	31±2.5	58.6	54.4

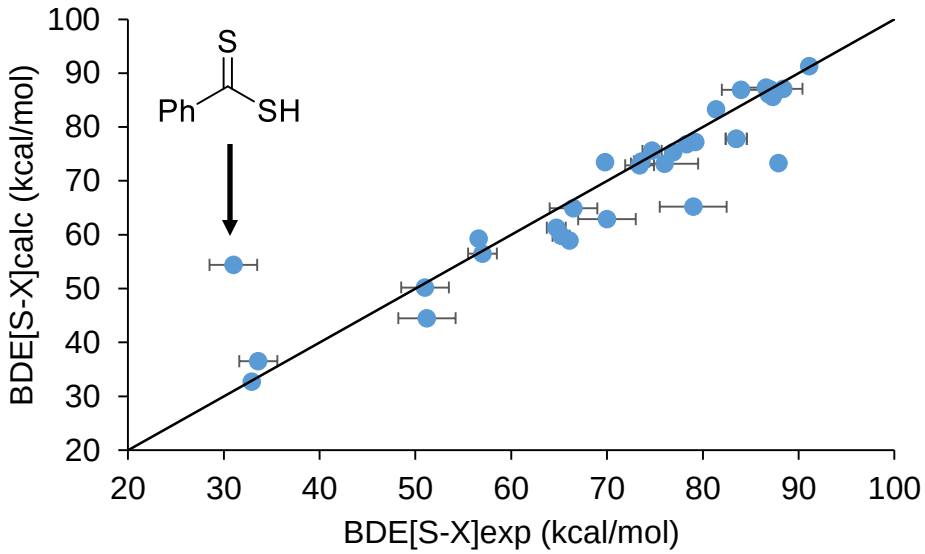
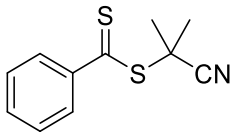


Figure 3.1 – Comparison of experimentally determined BDEs (BDE[S-X]exp) and calculated BDEs (BDE[S-X]calc). X=H, C, S, or Cl. The *y=x* line is included for clarity. Mean absolute deviation is 3.6 kcal/mol.

3.3 Dithioesters

Once it was determined that predicted BDEs were in good agreement with known values, calculations were performed on various dithioesters to determine their excited state energies and BDEs for radical formation. The compounds studied were 2-cyano-propyl benzodithioate (**34**), methy-2-((phenylcarbonothioyl)thiopropionate (**35**), and cyanomethyl benzodithioate (**36**) (Scheme 3.6). Compounds **34** and **36** were chosen as models for commercially available compound **16**. Compound **36** was used as a model compound to determine which bond cleavage is most likely to occur. Bond dissociation energies were calculated from vibrational energies determined at the (U)MN12SX/6-311G++(d,p)//(U)MN12SX/6-31G(d) level of theory. It was determined that the S-CH_2CN bond is the most labile of the bonds studied (Scheme 3.7).

Scheme 3.6 – Dithioesters used for calculations.



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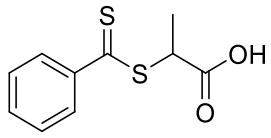

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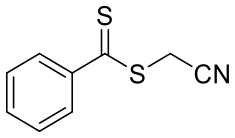

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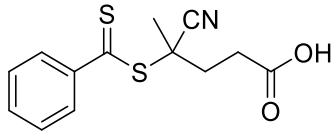

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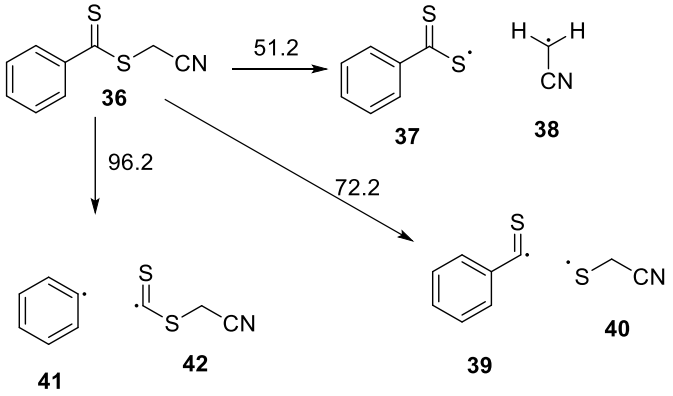
Scheme 3.7 - Possible RAFT agent fragmentations and their respective BDEs determined by (U)MN12SX/6-311G++(d,p)//(U)MN12SX/6-31G(d).



Computational modeling to determine the energy of higher singlets and triplets was carried out using **34**. Geometries were optimized at the (U)MN12SX/6-31G(d) level. Frequency calculations and vertical excitation energies were performed at the (U)MN12SX/6-311G++(d,p) level of theory. The results of these calculations can be seen in Table 3.4. The singlet-singlet transition energies and their respective wavelengths show good agreement with the absorption spectrum of **16**, a similar, commercially available dithioester (Figure 3.2).

Table 3.4 – Vertical excitation energies for **34**.

State	Energy[a] (kcal/mol)	Excitation Wavelength (nm)	State	Energy[b] (kcal/mol)	Excitation Wavelength[d] (nm)
S_0	0				
S_1	58.47	489.03	T_1	35.69[c]	
S_2	85.50	334.43	T_2	60.86	1136.22
S_3	89.87	318.14	T_3	84.85	581.64
S_4	93.24	306.64	T_4	86.69	560.68
S_5	93.81	304.77	T_5	90.91	517.85
			T_6	98.04	458.61
			T_7	99.50	448.09
			T_8	101.14	436.85
			T_9	104.33	416.54
			T_{10}	106.02	406.54
			T_{11}	107.64	397.39
			T_{12}	108.89	390.6
			T_{13}	110.92	380.1

[a]vertical energies at S_0 geometry [b]vertical energies at T1 geometry [c]adiabatic energy relative to S_0 [d]$T_1 \rightarrow T_n$

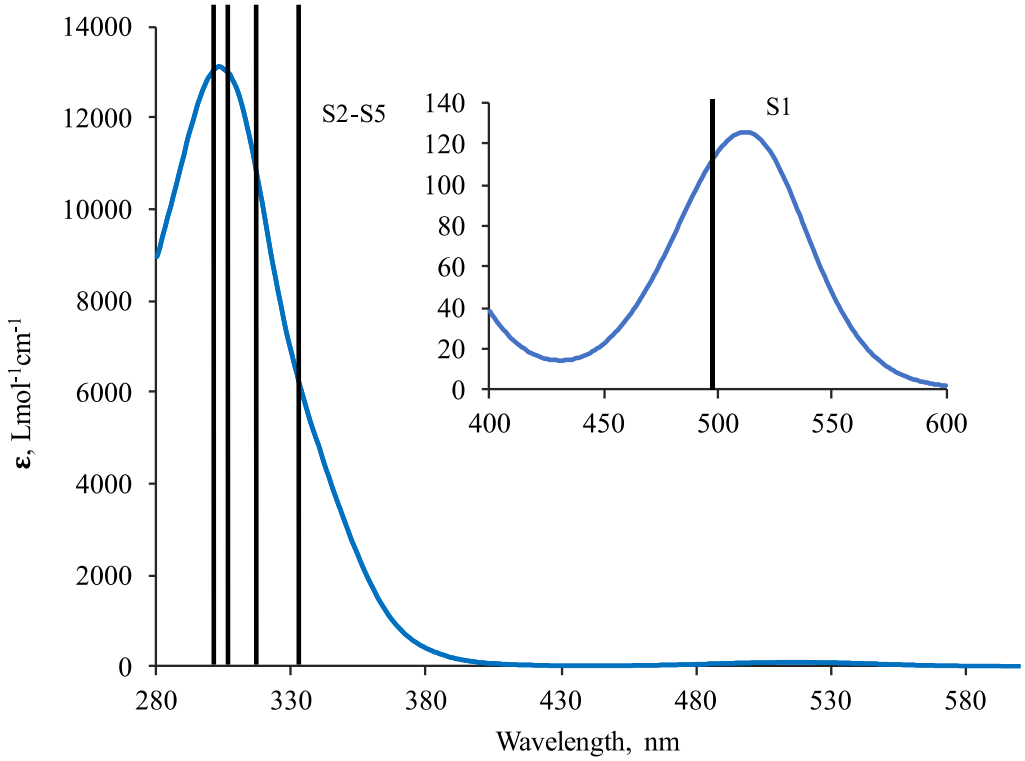


Figure 3.2 – UV-Vis absorption spectrum of **16** (blue) overlaid with singlet-singlet transitions calculated for model compound **34** (black). Figure provided by Matthew Thum.

The BDE for the S-C$(CH_3)_2$CN bond was determined by calculating the difference in energy between the S_0 state of **34** and the combined energy of the carbon-centered radical and the sulfur centered radical. The BDE was determined to be 41.4 kcal/mol (this BDE is much lower than the model due to increased stabilization of the carbon-centered radical from the two additional methyl groups). Notably, this energy is greater than the energy of the T_1 state implying that the lowest triplet is not responsible for formation of radicals and therefore is not likely to be responsible for initiation in a RAFT polymerization. It is possible, however, for dissociation from S_1 and T_2 (or other high energy singlets and triplets) (Figure 3.3). Consistent with these calculations, direct irradiation of the S_1 absorption band with a 100 mW 532 nm CW diode laser shows little decomposition of **34** after two hours whereas irradiation with a 100 mW 405 nm CW diode laser shows a significant change in absorbance in 30 minutes (Thum, unpublished). This result implies that excitation with 532 nm leads to formation of S_1 but that S_1 either does not produce radicals or that the conversion from S_1 to T_1 is relatively efficient and T_1 does not lead to radical formation. On the other hand, excitation with 405 nm excites the iniferter to the S_2 state which leads to radicals either directly or through T_2. Additionally, the predicted T_1 for model compound **34** is consistent with triplet quenching experiments for **16**. In the triplet quenching experiments shown in Table 3.5, the sensitizer triplet is monitored by LFP in the presence of various concentrations of **16**. Using a pseudo-first order analysis, a quenching rate can be determined for **16** with each sensitizer. Sensitizers, such as thioxanthone and acridine, with a triplet energy greater than that of **16** are quenched near the diffusion limit ($1x10^{10}$). As the triplet energy of the sensitizer decreases,

quenching becomes less efficient. Once a sensitizer with a triplet energy lower than **16** is used, quenching becomes extremely slow. This is observed in the case of methylene blue, where the triplet energy of the sensitizer (33.0 kcal/mol) is less than the triplet energy of **16** (predicted to be 35.7 kcal/mol) and very little quenching is observed.

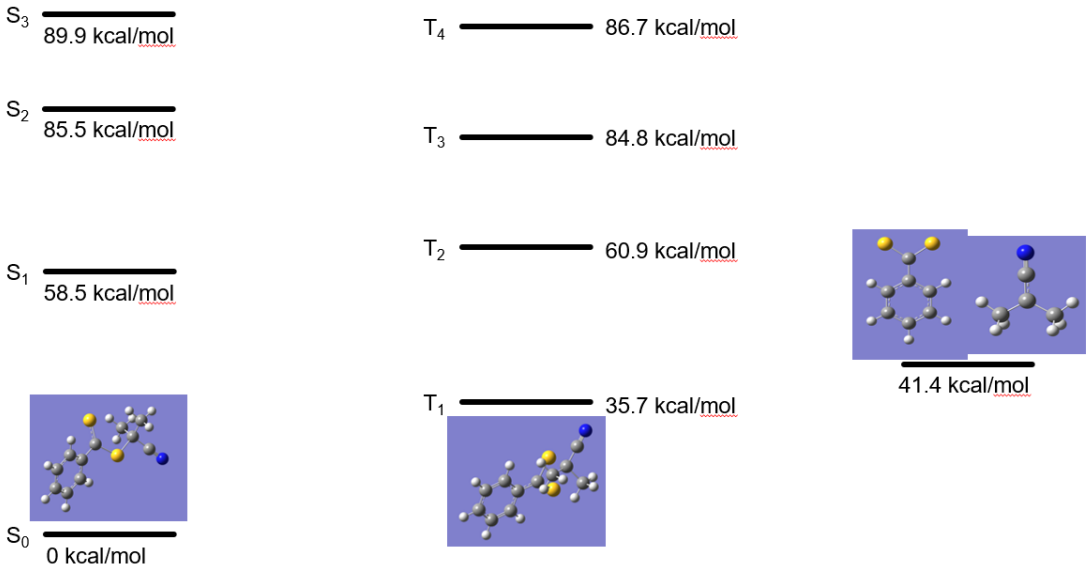


Figure 3.3 – Jabłoński diagram depicting the energy levels of **34**, its excited states, and likely radical products.

Similar to **34**, compound **35** has a T_1 energy lower than the energy necessary for bond cleavage. The BDE for **35** was determined to be 51.6 kcal/mol while the T_1 energy was only 37.3 kcal/mol. As with **34**, the S_1, T_2, and higher energy states of **35** do have sufficient energy to effect bond cleavage (Table 3.6).

Table 3.5 – Quenching of sensitizers with **16**. Provided by Matthew Thum.

Sensitizer	Triplet Energy[88] (kcal/mol)	Quenching Rate ($M^{-1}s^{-1}$)
Thioxanthone[a]	63.3	$7.86x10^9$
Acridine[b]	45.0	$1.93x10^9$
Eosin Y[c]	42.3	$3.31x10^8$
Rose Bengal[b]	41.5	$5.31x10^8$
Zinc-Tetraphenyl Porphine[b]	36.6	$1.4x10^8$
Methylene Blue[b]	33.0	$<1x10^6$

[a]Measured in benzene [b]Measured in MeCN [c]Measured in 3:2 ethanol:water

Table 3.6 – Vertical excitation energies for **35**.

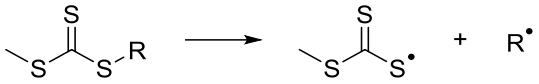
State	Energy[a] (kcal/mol)	Excitation Wavelength (nm)	State	Energy[b] (kcal/mol)	Excitation Wavelength[d] (nm)
S_0	0				
S_1	60.45	473.02	T_1	37.32[c]	
S_2	81.07	352.68	T_2	62.51	1134.94
S_3	84.33	339.05	T_3	85.57	592.54
S_4	89.42	319.74	T_4	88.44	559.22
S_5	92.25	309.94	T_5	88.82	555.18
			T_6	92.70	516.24
			T_7	97.32	476.47
			T_8	98.99	463.58
			T_9	102.71	437.24
			T_{10}	103.29	433.37
			T_{11}	105.54	419.08
			T_{12}	107.47	407.54
			T_{13}	108.18	403.48

[a]vertical energies at S_0 geometry [b]vertical energies at T1 geometry [c]adiabatic energy relative to S_0 [d]$T_1 \rightarrow T_n$

3.4 Trithiocarbonates

Trithiocarbonates have garnered a good deal of attention in recent literature.[97,104,118,131–134] To determine the means by which trithiocarbonates make radicals, calculations were done on model compounds to identify BDEs and excited state energies. Based on the initial models used, it seems that trithiocarbonates follow the same trend as the dithioesters: their T_1 energy is ten to fifteen kcal/mol lower than their respective BDEs (Table 3.7).

Table 3.7 – Calculated BDEs and excited state energies for trithiocarbonate models.



41 **42**

R=	BDE (kcal/mol)	T_1 Energy[b] (kcal/mol)	S_1 Energy[a] (kcal/mol)	S_2 Energy[a] (kcal/mol)
$-CH_3$	66.5	52.2	73.7	84.8
$-CH_2CH_3$	64.6	52.3	72.9	85.0
$-CH(CH3)_2$	59.0	48.4	70.5	81.2
$-C(CH_3)_3$	57.2	47.6	70.9	81.5

[a]vertical energies at S_0 geometry [b]adiabatic energy relative to S_0

The mechanism for polymerization using trithiocarbonates is similar to that of the dithioesters. A proposed mechanism for multicolor photo-RAFT polymerization using a popular trithiocarbonate, dibenzyltrithiocarbonate (**43**), is shown in Scheme 3.8. In the first step, the RAFT agent is irradiated with broadband UV-visible light eventually generating a sulfur-centered radical and a benzyl radical (I). Then, the benzyl radical initiates polymerization by adding to monomer. The growing polymer chain is then capped by the sulfur-centered radical (II). The process repeats with dormant polymer chain become excited via multiphoton irradiation and generating a

new sulfur-centered radicals and an additional benzyl radical (III). The benzyl radical can initiate growth of a new polymer chain that is capped by the sulfur-centered radical (IV). The disubstituted trithiocarbonate then undergoes the main RAFT process.

Calculations were performed on **43**, to determine if, like the model trithiocarbonates, its BDE for radical formation is above the energy of its lowest triplet. The BDE for **43** is in fact lower than its T_1 state but only by c. 2 kcal/mol (Table 3.8). This indicates that it may be possible for **43** to generate radicals from T_1 (and higher triplets) in addition to S_1 (and higher singlets).

Scheme 3.8 – General mechanism of RAFT polymerization using **43**.[131]

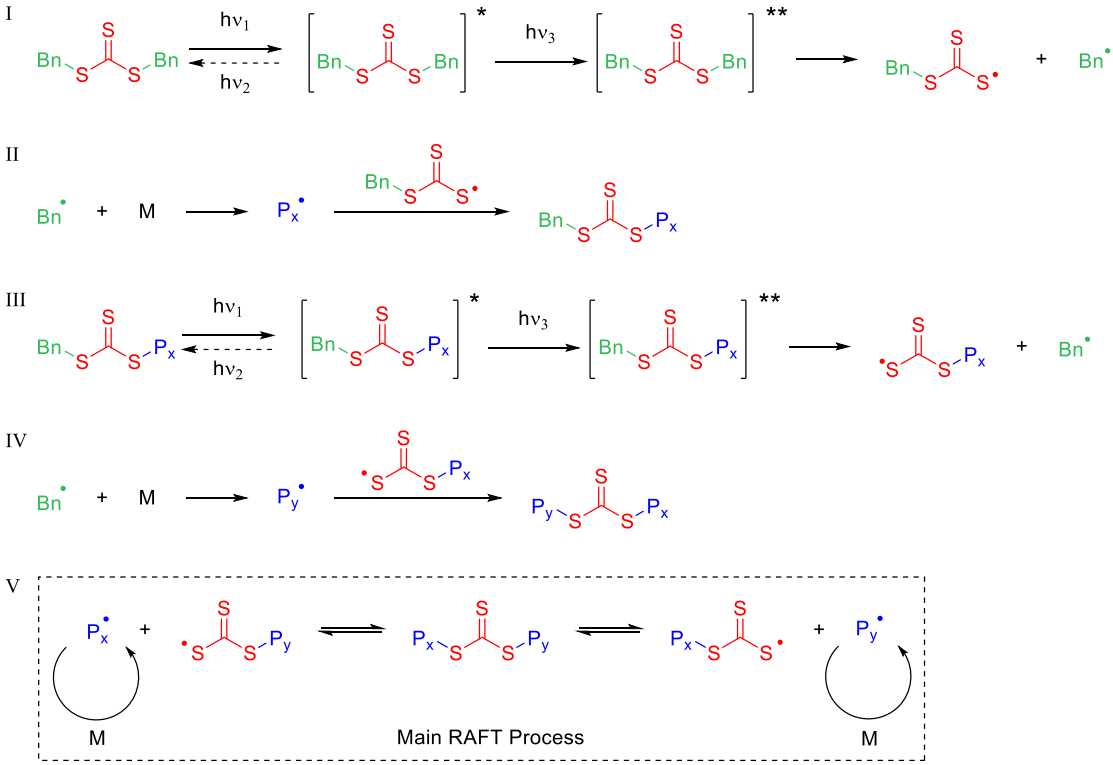
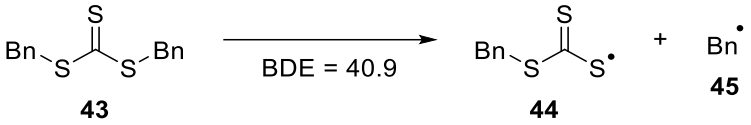


Table 3.8 – Vertical excitation energies for **43**.



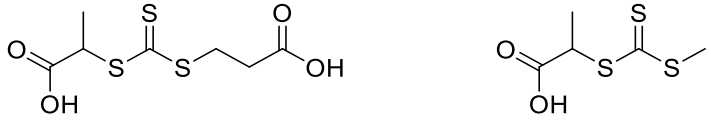
43 **44** **45**

State	Energy[a] (kcal/mol)	Excitation Wavelength (nm)	State	Energy[b] (kcal/mol)	Excitation Wavelength[d] (nm)
S_0	0				
S_1	55.78	512.61	T_1	38.89[c]	
S_2	74.89	381.77	T_2	70.44	906.19
S_3	81.30	351.68	T_3	72.13	860.3
S_4	84.26	339.33	T_4	75.76	775.49
S_5	84.61	337.92	T_5	90.05	558.83
			T_6	91.27	545.89
			T_7	93.85	520.29
			T_8	95.24	507.44
			T_9	95.40	505.97
			T_{10}	95.41	505.85
			T_{11}	97.88	484.71
			T_{12}	101.06	459.91
			T_{13}	101.83	454.28

[a]vertical energies at S_0 geometry [b]vertical energies at T_1 geometry [c]adiabatic energy relative to S_0 [d]$T_1 \rightarrow T_n$

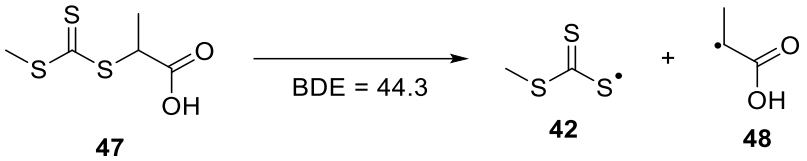
Another common trithiocarbonate RAFT agent is 3-((((1-carboxyethyl)thio)carbonothioyl)thio)propanoic acid, **46**.[135,136] Calculations were performed on the model compound 2-(((methylthio)carbonothioyl)thio) propanoic acid, **47**, to save computer time (Scheme 3.9). These calculations on **30** show that its T_1 (39.5 kcal/mol) is c. 5 kcal/mol lower in energy than the BDE (44.3 kcal/mol) for radical formation (Table 3.9).

Scheme 3.9 – **46** and the model compound used for calculations.



46 **47**

Table 3.9 – Vertical excitation energies for **47**.



47 **42** **48**

State	Energy[a] (kcal/mol)	Excitation Wavelength (nm)	State	Energy[b] (kcal/mol)	Excitation Wavelength[d] (nm)
S_0	0				
S_1	59.23	482.68	T_1	39.48[c]	
S_2	84.61	337.94	T_2	74.43	818.05
S_3	92.46	309.23	T_3	77.70	748.15
S_4	94.02	304.11	T_4	80.29	700.61
S_5	96.39	296.64	T_5	105.68	431.91
S_6	96.88	295.12	T_6	105.92	430.31
			T_7	109.68	407.3
			T_8	112.12	393.61
			T_9	114.11	383.1
			T_{10}	114.23	382.5
			T_{11}	119.29	358.23
			T_{12}	124.05	338.08
			T_{13}	126.17	329.83

[a]vertical energies at S_0 geometry [b]vertical energies at T1 geometry [c]adiabatic energy relative to S_0 [d]$T_1 \rightarrow T_n$

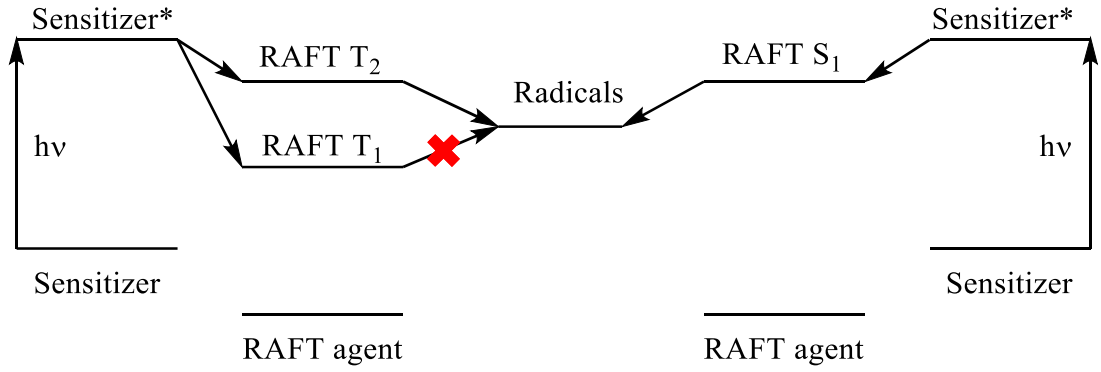
3.5 Conclusions

Since the photophysics of many RAFT agents are mostly unknown, computational chemistry can be a powerful tool for understanding the initation mechanism for iniferters. Calculations performed with (U)MN12SX can accurately predict the bond dissociation energies of dithio- and trithio-compounds as well as excited state energies for the corresponding compounds. Calculations performed on dithioesters show that their T_1 states do not have sufficient energy to effect a bond cleavage. Instead, it appears that the dithioesters generate radicals via S_1, T_2, or higher energy states. On the other hand, calculations for trithiocarbonates show that their BDEs might be low enough that T_1 can form radicals and initiate polymerization.

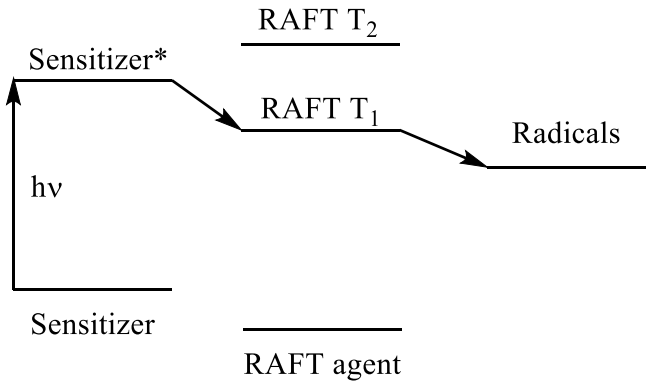
Energy transfer agents where a separate sensitizer is used to generate T_1 independent of S_1 should reveal more about the manner in which RAFT agents generate radicals (Scheme 3.10).

Scheme 3.10 – Proposed energy transfer experiments for RAFT agents. A – Sensitization to the T_2 or S_n states of dithioesters may generate radicals revealing the mechanism of radical formation. B – Sensitization to the T_1 state of trithiocarbonates may result in radical formation directly from the lowest triplet.

A)



B)



Chapter 4: Photogeneration of Acids by Direct Irradiation of 2-methoxy-9,10-dioxo-9,10-dihydroanthracen-1-yl 4-methylbenzenesulfonate

4.1 Introduction to 2-methoxy-9,10-dioxo-9,10-dihydroanthracen-1-yl 4-methylbenzenesulfonate

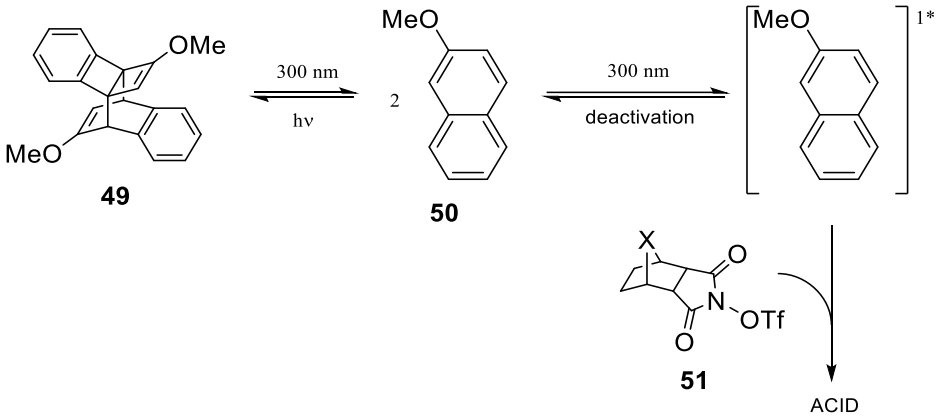
Photoacid generators (PAGs) are compounds that, upon irradiation, undergo reactions to produce acid.[137] Common PAGs include onium salts,[138–140] sulfonium salts,[139,141] sulfonate esters,[142,143] imino esters,[144,145] and spiropyrans.[146–149] PAGs have been used in a wide variety of areas such as for biological applications,[150] photodynamic therapy,[151] protecting group chemistry,[152,153] and polymerization initiation.[28,154,155]

Due to the enhanced spatial control afforded by two-photon chemistry, a two-photon PAG could provide improved resolution for photolithography. Photochemical production of acid can be attractive for both positive- and negative-tone photoresists. In a positive-tone resist, the acid generated by the PAG can be used to enhance solubility in illuminated regions. In a negative-tone resist, the acid is often used to initiate polymerization.[28,137]

Sulfonates are a popular choice for use as PAGs.[142,143,156–159] Sulfonates have previously been identified as photolabile groups in 1968 when Zen et al. first reported the photochemical detosylation of sugars.[160] Many of these modern systems rely on the same principle, now making use of the sulfonic acid generated rather than discarding it as a byproduct. These sulfonic acid generators produce sulfonic acids via homolysis of an O-N bond.[156] Homolysis generates a sulfonyl radical which undergoes hydrogen atom abstraction to generate a sulfonic acid which in turn catalyzes cationic

polymerization. These PAGs use a single wavelength of UV or short wavelength visible light to produce acid. Turro and coworkers propose a strategy for two-photon generation of sulfonic acid that incorporates an external sensitizer.[158] In Turro's scheme, the external sensitizer is activated by the sequential absorbance of two photons and undergoes an electron transfer to the PAG, ultimately generating acid. The first step in this scheme is excitation of the latent sensitizer, **49**, a dimer of the active sensitizer, **50**, by a 300 nm photon to yield two equivalents of the active sensitizer. The active sensitizer also absorbs 300 nm light to give the excited sensitizer. The excited sensitizer can transfer an electron to the PAG, **51**, causing a reaction that produces acid (Scheme 4.1).

Scheme 4.1 – Turro's sequential two-photon PAG system.



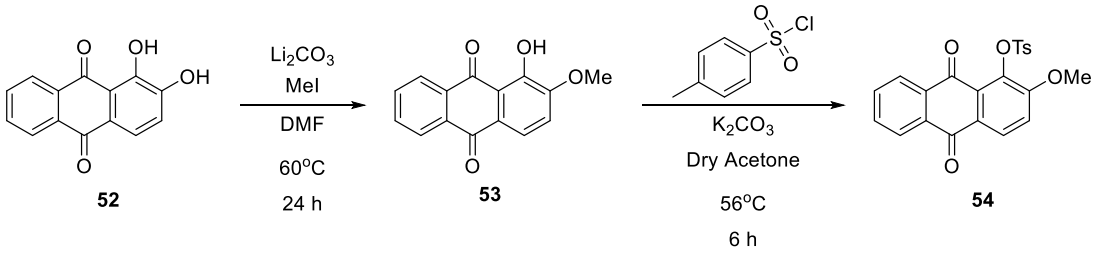
This chapter will explore two-photon PAGs that employ two different wavelengths of light. The PAG explored here is 2-methoxy-9,10-dioxo-9,10-dihydroanthracene-1-yl-tosylate (**54**). Compound **54** generates *p*-toluenesulfonic acid (*p*-TsOH) upon illumination with 355 nm light. Compound **54** also demonstrates enhanced acid generation when irradiated with 355 and 532 nm light simultaneously,

indicative of a two-photon process. Preliminary results for 1-acyloxy-2-methoxyanthraquinone-based PAGs are also reported.

4.2 Synthesis and Physical Properties

Compound **54** can be synthesized in two steps from commercially available 1,2-dihydroxyanthraquinone, also known as alizarin, **52**. Treatment of **52** with iodomethane and lithium carbonate in dimethylformamide preferentially alkylates the 2-position of the anthraquinone yielding alizarin methyl ether, **53**. **53** can be produced on a gram-scale in excellent yields (94%) and exhibits as strong absorbance in the visible spectrum (λ_{max}=425 nm). Compound **53** is dissolved in dry acetone along with potassium carbonate. Tosyl chloride is added and the reaction mixture is refluxed for 6 h yielding **54** (37%) (Scheme 4.2).

Scheme 4.2 – Synthesis of **54**.



Compound **54** has one λ_{max} c. 333 nm and another c. 358 nm. The absorbance of **54** tails into the visible region up to c. 450 nm (Figure 4.1). Laser flash photolysis of **54** shows a transient species with strong absorbance in the visible region with peaks c. 470 and 600 nm (Figure 4.2). These peaks are consistent with experimental results from the literature showing anthraquinone derivatives with triplet-triplet absorption c. 450 and 550 nm.[162,163] Additionally, computational results for similar anthraquinone derivatives in the literature predict transitions at 465 and 580 nm.[164] The decay of the transient fits a first-order model, with a decay constant of 5.8×10^5 s^{-1} and a half-life of

1.7 µs. Also, the transient is quenched by oxygen (Figure 4.2, inset). Along with the literature data for other functionalized anthraquinones, these data suggest that the observed transient is the triplet. The strong absorbance of the **54** ground state at 355 nm and the strong absorbance of the triplet at 532 nm could allow for two photon chemistry using a Nd:YAG laser.

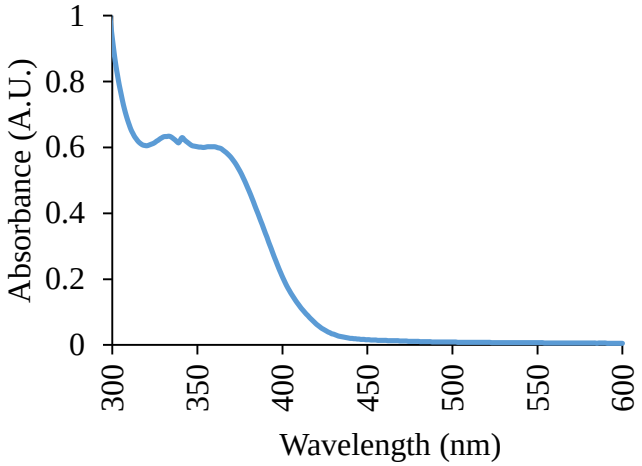


Figure 4.1 – UV-Vis absorbance of **54** in dimethyl sulfoxide.

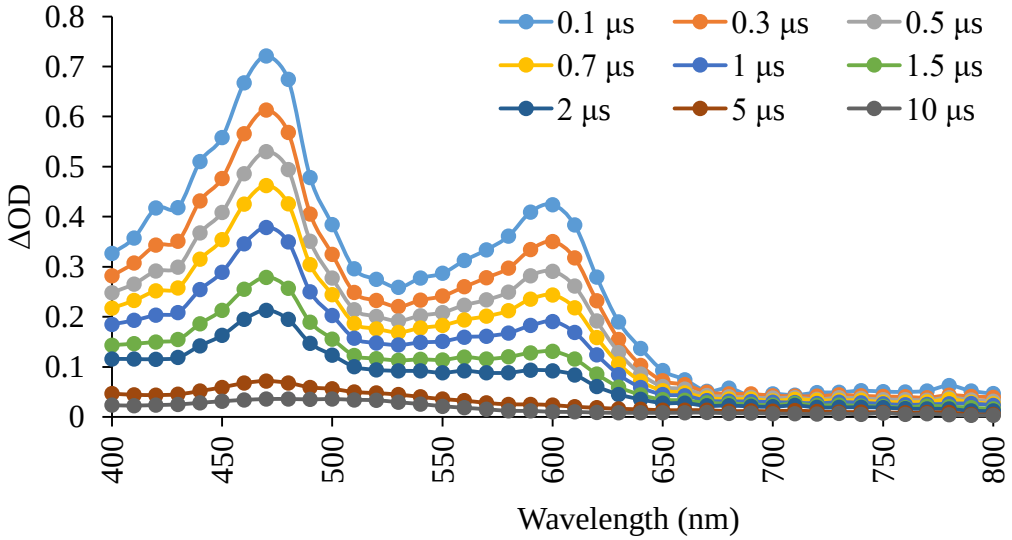


Figure 4.2 – Transient of **54** in acetonitrile (Ex: 355 nm).

4.3 Steady State Photolysis

A solution of **54** in dimethyl sulfoxide-d6 was irradiated with 355 nm light. ^{1}H-NMR spectra were collected before and after irradiation (Figure 4.3). After 30 minutes of photolysis the **54** appears to be completely converted. Peaks consistent *p*-TsOH and **53** are observed after photolysis in roughly the same yield relative to one another. Signals corresponding to **53** (*) and *p*-TsOH (♦) are labeled in Figure 4.3.

To better understand the effects of 355 and 532 nm light on the decomposition of **54**, 2 ml samples of 240 µM **54** in acetonitrile were prepared, sealed in cuvettes, purged with nitrogen and irradiated with various combinations of light. These photolyses were monitored using UV-Vis spectroscopy, specifically at 460 nm where **54** does not absorb light, but photoproduct **53** does absorb light. Samples were irradiated with 355 nm light alone, with 355 and 532 nm light, or with 532 nm light alone. A cylindrical lens was used to modify the beam shape. Beam overlap was optimized spectroscopically. For each sample, the change in absorbance at 460 nm (ΔA) was measured, normalized ($\Delta A/\Delta A_0$), and plotted against photolysis time (Figure 4.4). Linear fitting for the 355 nm experiments and the 355 + 532 nm experiments showed that formation of **53** was c. 55% faster with 532 nm light added than with 355 nm light alone. 532 nm light alone had no effect in the same time. An increase in the rate of formation of **53** with the addition of 532 nm light is consistent with a two-photon mechanism. The observed photolysis with 355 nm light alone could be due to either a one-photon background process or a two-photon process utilizing two 355 nm photons.

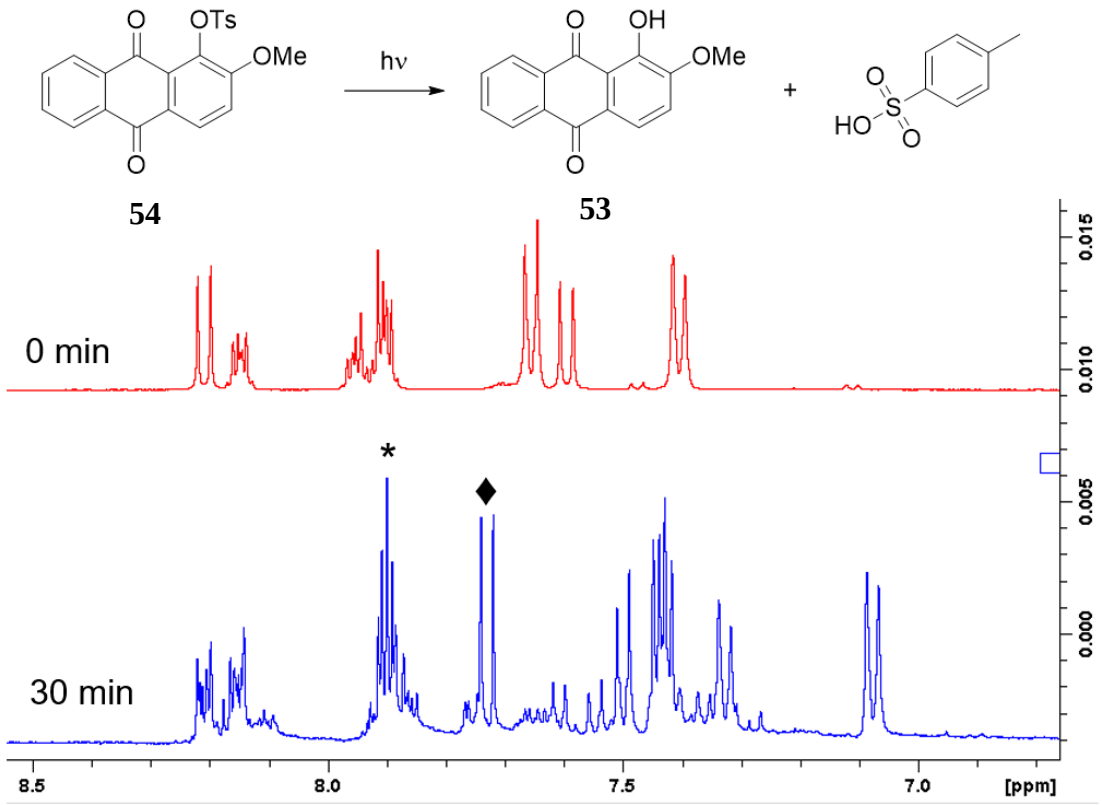


Figure 4.3 – Photolysis of **54** in dimethyl sulfoxide-d6 monitored by ^{1}H-NMR.

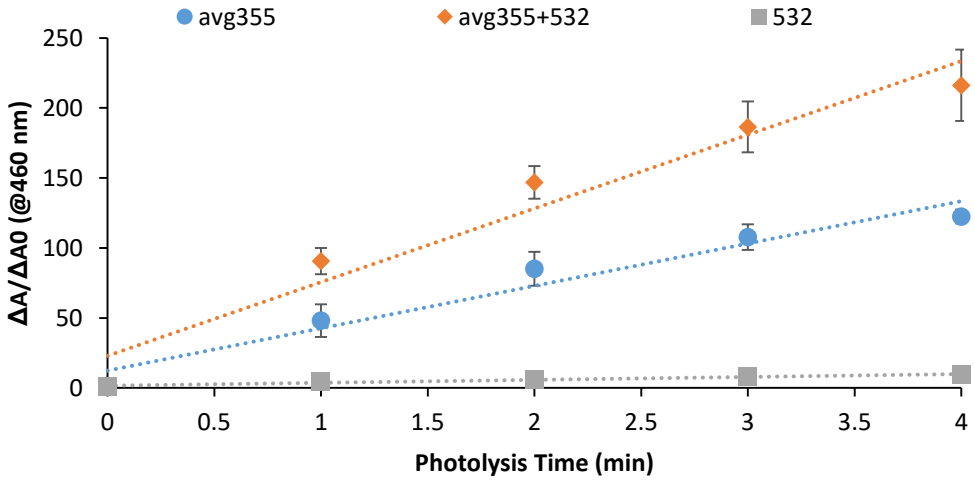


Figure 4.4 – Photolysis of **54** in MeCN with 355 nm (●), 355 + 532 nm (♦), and 532 nm (■). Photolysis was performed using the first and second harmonics of a Nd:YAG laser operating at 10 Hz. The power of the 355 nm beam was 10-13 mJ/pulse and the power of the 532 nm beam was 81-90 mJ/pulse. 355 nm and 355 + 532 nm experiments were done in duplicate. Error bars indicate one standard deviation of duplicate experiments.

To optimize the amount of *p*-TsOH produced by photolysis of **54**, 1 ml samples of **54** in MeCN-d3 were prepared in cuvettes. These samples were irradiated under aerobic conditions using a Nd:YAG laser operating at 10 Hz. Samples were irradiated with 355 and 532 nm light. The 355 and 532 nm beams were aligned so that the beams were coincident. After photolysis, samples were analyzed by ^{1}H-NMR (Figure 4.5). Peaks corresponding to **54** and *p*-TsOH were integrated and calibrated relative to the solvent signal. *p*-TsOH production was observed after only two minutes of photolysis (Figure 4.6). Acid production continues until c. eight minutes where the percent yield of *p*-TsOH reaches a maximum of c. 72%. At eight minutes, conversion of **54** had reached only 87%. The photolysis was continued until 12 minutes, when conversion reached 100%. Unfortunately, at 12 minutes the yield of acid had decreased from 72% to 68%, possibly due to decomposition as a result of over photolysis. To maximize yield and conversion, ten minutes was chosen as the photolysis time for **54**.

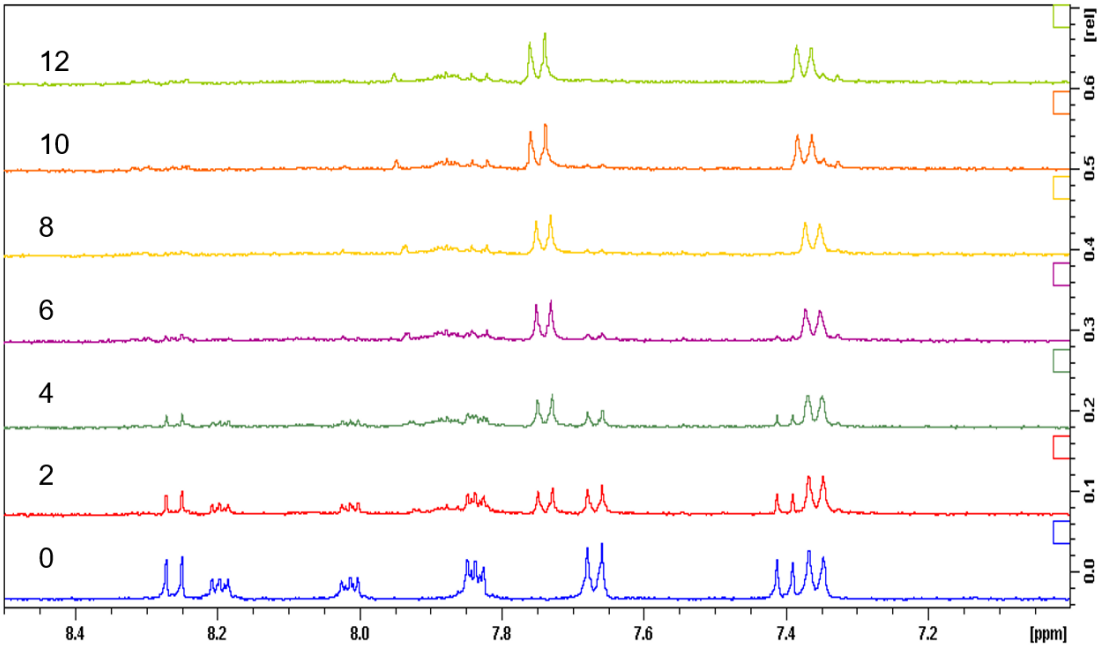


Figure 4.5 – ^{1}H-NMR spectra of **54** in MeCN-d3 photolyzed with 355 and 532 nm for the specified times. Experiments were performed in cuvettes with an air atmosphere using a Nd:YAG laser operating at 10 Hz. The 355 nm power was 8-10 mJ/pulse and the 532 nm power was 87-89 mJ/pulse.

To determine the impact of 532 nm light on *p*-TsOH production, 1 ml samples of **54** in MeCN-d3 were prepared in cuvettes. These samples were irradiated under aerobic conditions using a Nd:YAG laser operating at 10 Hz. Samples were irradiated with 355 nm light alone, with 355 and 532 nm light, or with 532 nm light alone. The 355 and 532 nm beams were aligned such that, when active simultaneously, the beams were coincident. After photolysis, samples were analyzed by ^{1}H-NMR. Peaks corresponding to **54** and *p*-TsOH were integrated and calibrated relative to the solvent signal. The results of these photolysis reactions can be seen in Table 4.1. With only 355 nm light (entry 1), only c. 34% of *p*-TsOH was released. The combination of 355 and 532 nm light (entry 2) more than doubled the amount of *p*-TsOH, c. 77% overall.

Irradiation with 532 nm light alone (entry 3) failed to produce any *p*-TsOH. A dark control (entry 4) similarly did not generate any release.

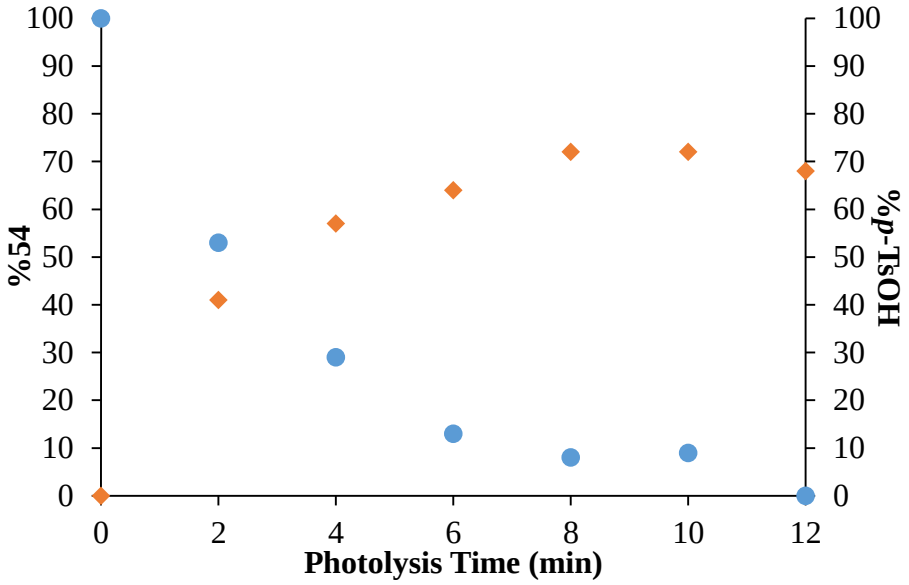


Figure 4.6 – Time course photolysis of **54** (240 µM) in MeCN-d3. Conversion of **54** (●) and yield of *p*-TsOH (♦) calculated as the average of three experiments and represented as a percent. Error bars represent one standard deviation of triplicate experiments. Experiments were performed in cuvettes with an air atmosphere using a Nd:YAG laser operating at 10 Hz. The 355 nm power was 8-10 mJ/pulse and the 532 nm power was 87-89 mJ/pulse.

Table 4.1 – Yield of *p*-TsOH release following photolysis of **54** in MeCN-d3 as analyzed by ^{1}H-NMR.

Entry	355 nm Power [mJ/pulse]	532 nm Power [mJ/pulse]	Photolysis Time (min)	%Conversion	%Yield
1	9-11	0	10	58±17[a]	34±10[a]
2	8-10	87-90	10	94±3[a]	77±11[a]
3	0	87-90	10	0	0
4	0	0	-	0	0

[a]Conversion and yield are reported as the average of triplicate experiments, error is reported as standard deviation of triplicate experiments.

Investigations into the mechanism of *p*-TsOH release are still underway, but some key insights have led to a proposed excited state homolysis mechanism. In collaboration with Andrea Zeppuhar, it was observed that **53** is formed only in samples

photolyzed in a nitrogen atmosphere, but with low yields of *p*-TsOH. In oxygen, **53** is not observed, but *p*-TsOH is produced in high yields (Figure 4.7). The lack of *p*-TsOH formation in nitrogen-purged solutions may be due to the formation of sulfinic acid in solution (Scheme 4.3 – A). Sulfinic acid generation from aryl tosylates in nitrogen atmosphere has been previously reported.[165] In oxygen, the absence of **53** has been attributed to reactions with dissolved oxygen to form various degradation products. No degradation products have been isolated. Photolysis in the presence of oxygen with 1,4-cyclohexadiene (CHD) shows the formation of **53** (Figure 4.8).

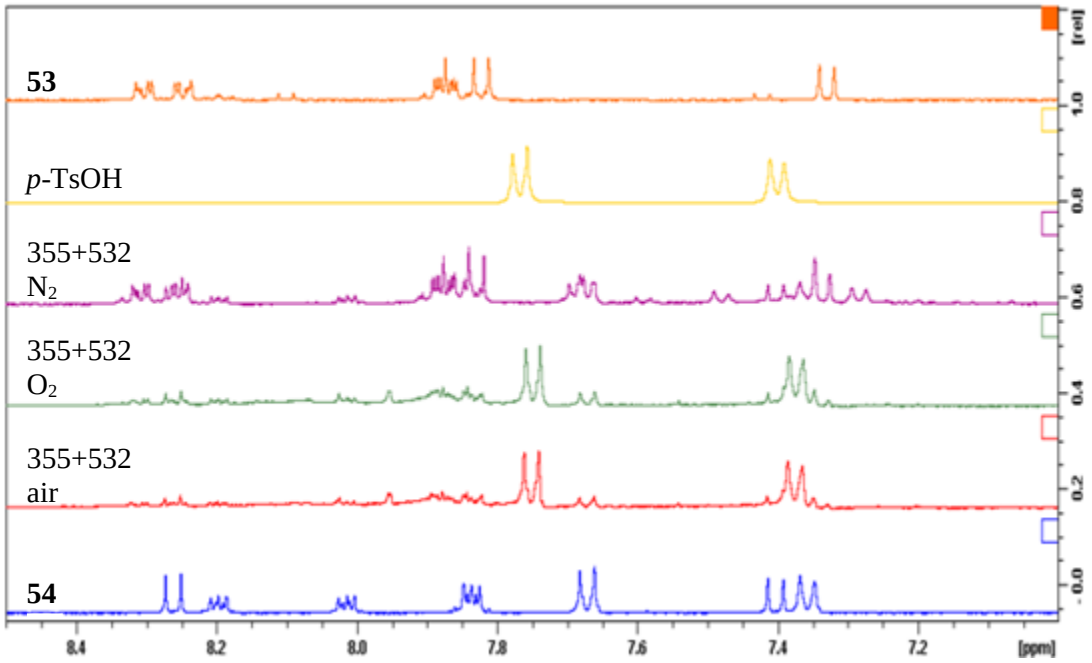


Figure 4.7 – Photolysis of **54** in air and nitrogen atmospheres. Performed in MeCN-d3 using 355 nm light (8-10 mJ/pulse) and 532 nm (88-90 mJ/pulse) from a Nd:YAG laser operating at 10 Hz monitored by ^{1}H-NMR. Figure provided by Andrea Zeppuhar.

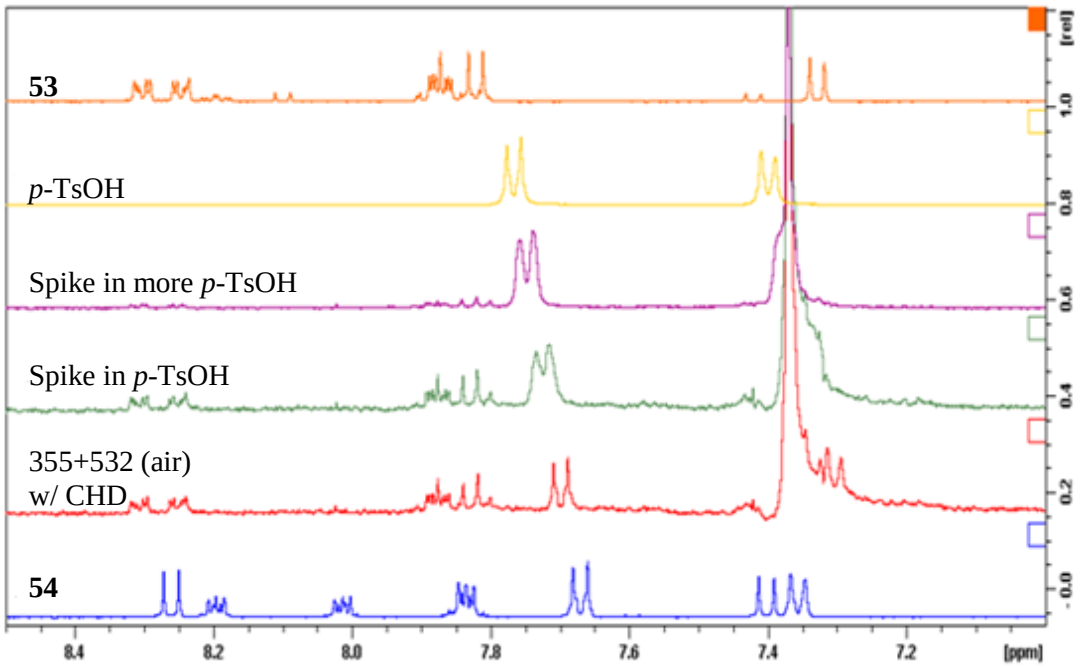
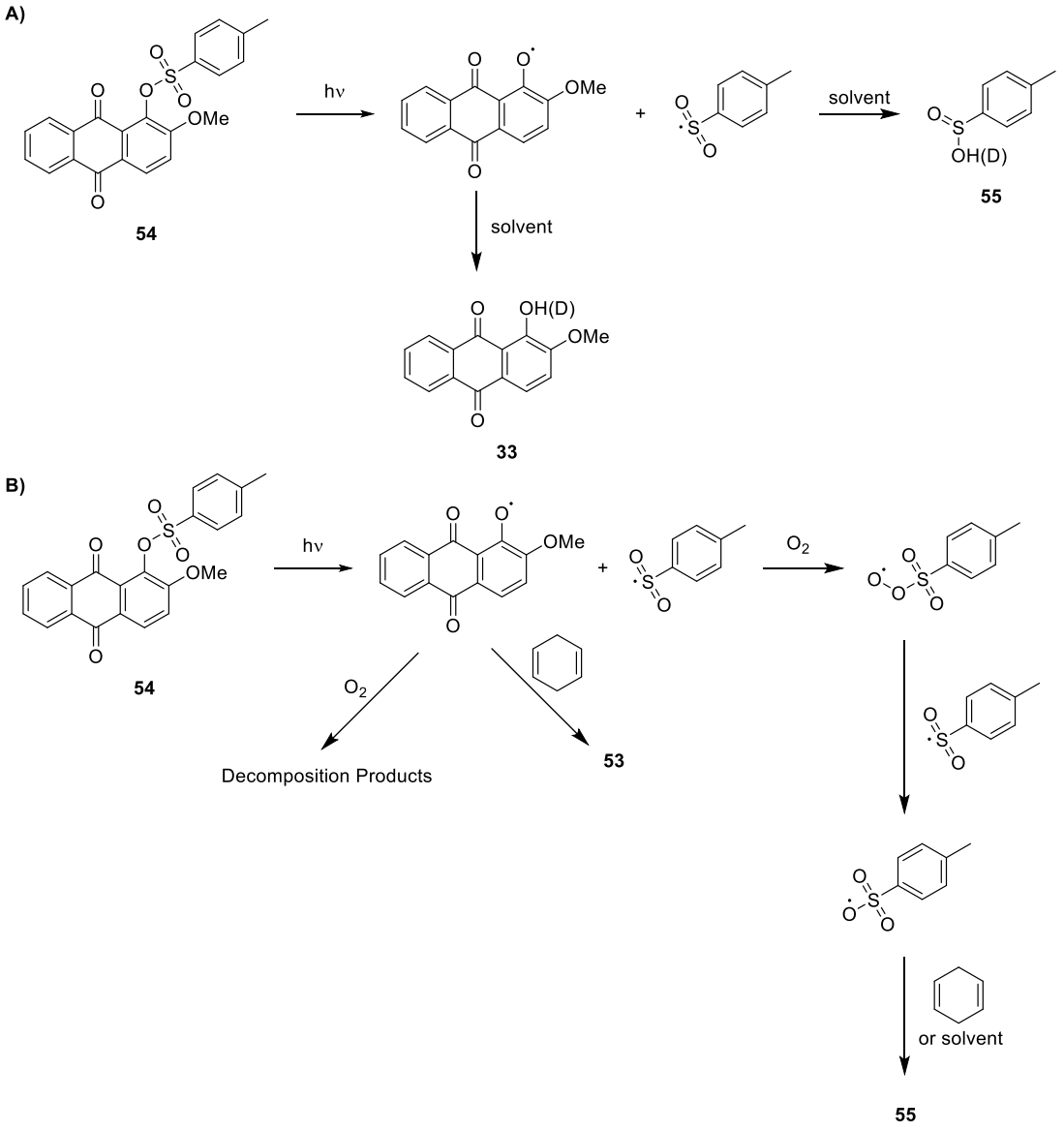


Figure 4.8 – Photolysis of **54** in MeCN with 1,4-cyclohexadiene. Performed in MeCN-d3 under an air atmosphere using 355 nm light (9-11 mJ/pulse) and 532 nm (86-87 mJ/pulse) from a Nd:YAG laser operating at 10 Hz monitored by ^{1}H-NMR. *p*-TsOH was spiked into the photolysis multiple times to confirm production. Figure provided by Andrea Zeppuhar.

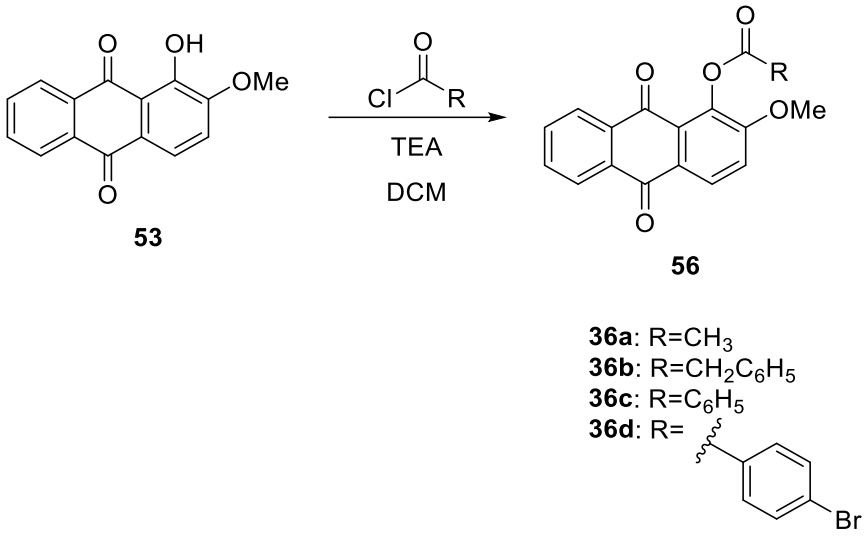
Scheme 4.3 – Proposed mechanism for *p*-TsOH release for **54**.



4.4 2-Methoxyanthraquinone Esters

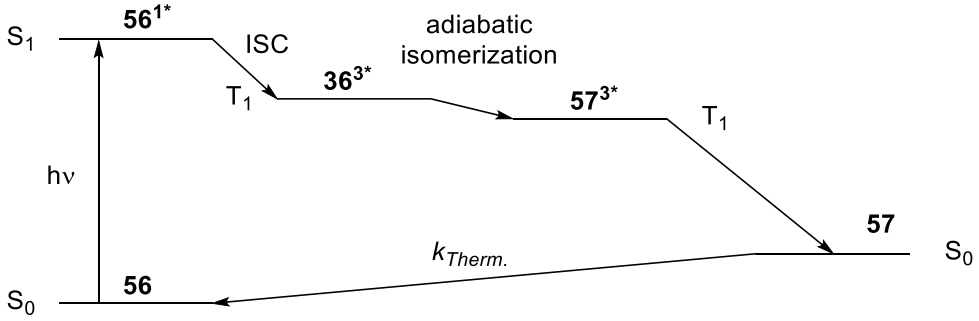
2-methoxyanthraquinone esters (MAEs) are synthesized from alizarin methyl ether **53**. Compound **53** is dissolved in dichloromethane (DCM) and triethylamine (TEA) is added to the solution. MAEs **56a-d** are obtained by treatment with the corresponding acyl chloride (Scheme 4.4).

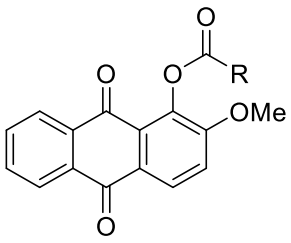
Scheme 4.4 – Synthesis of MAEs.



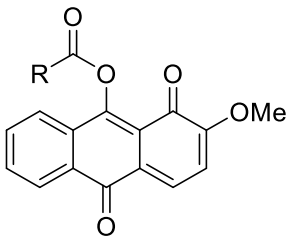
MAEs are well represented in literature for their photochemical acyl migration process (Scheme 4.5).[164,166–169] This process is described as an adiabatic *trans-ana* isomerization. Upon absorption of a photon, the ground state *trans* form, **56**, is promoted to its singlet excited state, $\mathbf{56}^{1*}$. This singlet can undergo intersystem crossing to form the excited *trans* triplet, $\mathbf{56}^{3*}$. $\mathbf{56}^{3*}$ undergoes an adiabatic isomerization where the acyl group migrates from the oxygen at the 1 position to the oxygen at the 9 position, giving the triplet of the *ana* form, $\mathbf{57}^{3*}$. Triplet *ana* can relax to form ground state *ana*, **57**, which can thermally revert to ground state *trans*, **56**. The *trans-ana* isomerization is unusual among photochemical reactions in that it is adiabatic. Additionally, the isomerization proceeds along the triplet potential energy surface.[169] MAEs might provide improved control among photoacid generators if the *ana* form does not lead to acid production. The MAEs could be excited to their triplet state then either deactivated by one wavelength or further activated to produce acid.

Scheme 4.5 – Photochemical isomerization of MAEs.





56



57

Transient absorption spectroscopy was performed on **56a** using laser flash photolysis (LFP). The transient spectrum shows two different species (Figure 5.8). The peak c. 390 nm fits to a second-order decay with a decay constant of 5.1×10^6 $M^{-1}s^{-1}$. The peak c. 480 nm contains a growth region and a decay region. The growth portion of the signal is first-order with a growth constant of 1.9×10^7 s^{-1}. The decay portion of the signal at 480 nm is first-order with a decay constant of 5.4×10^5 s^{-1}.

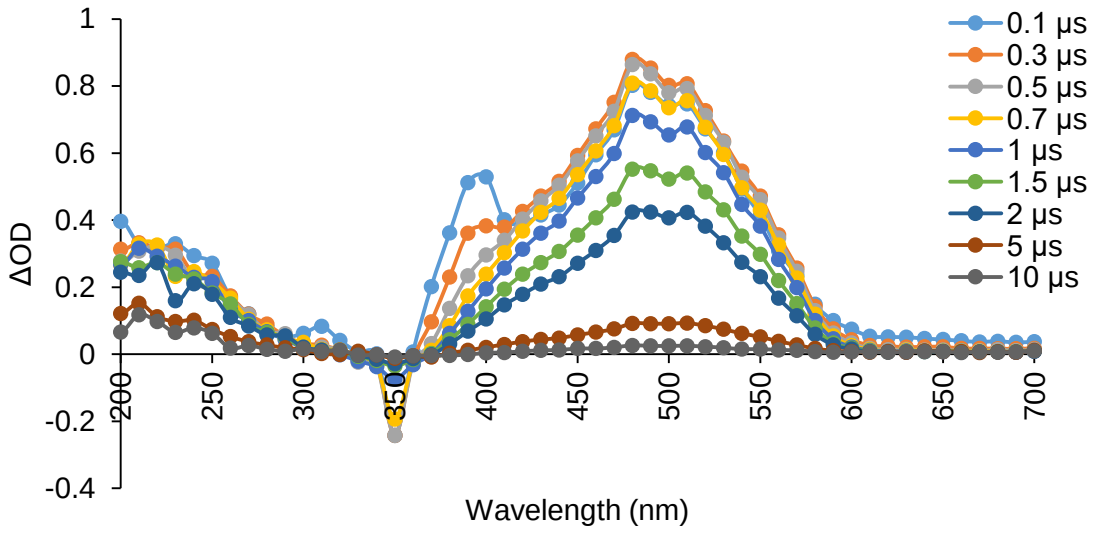


Figure 4.9 – Transient absorption spectrum of **56a** in MeCN (Excitation at 355 nm).

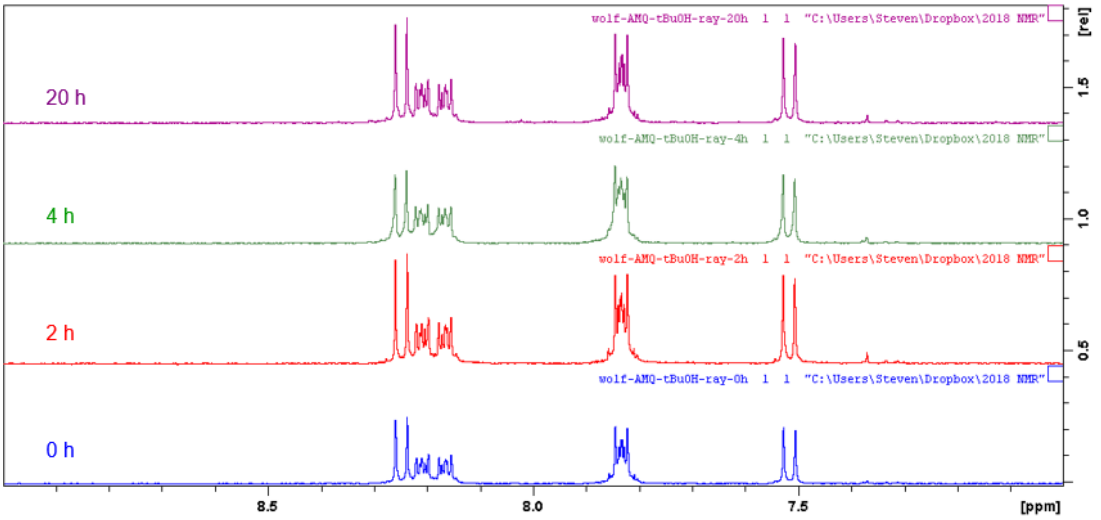


Figure 4.10 – Photolysis of **56a** in MeCN-d3 using a 16-bulb Rayoned photoreactor monitored by ^{1}H-NMR. 2-methyl-2-propanol was used as an internal standard for calibration and integration.

To compare light sources, **56a** was dissolved in deuterated acetonitrile with 2-methyl-2-propanol added as an internal standard. The first sample was photolyzed in a glass vial with 350 nm broadband irradiation from a 16-bulb Rayonet photoreactor. The results of this photolysis can be seen in Figure 4.10. There is no apparent change in the

sample after 20 hours of irradiation. The second sample of **56a** was photolyzed in a glass vial with a magnetic stir bar. The mixture was stirred while photolyzed at 355 nm using the second harmonic of a Nd:YAG laser (10 Hz, 82-83 mJ/pulse). As seen in Figure 4.11, **56a** is almost completely consumed after 50 minutes of irradiation, a dose equivalent to 20 hours of photolysis with the less intense Rayonet. The dramatic difference in photolysis rates is consistent with a two-photon process.

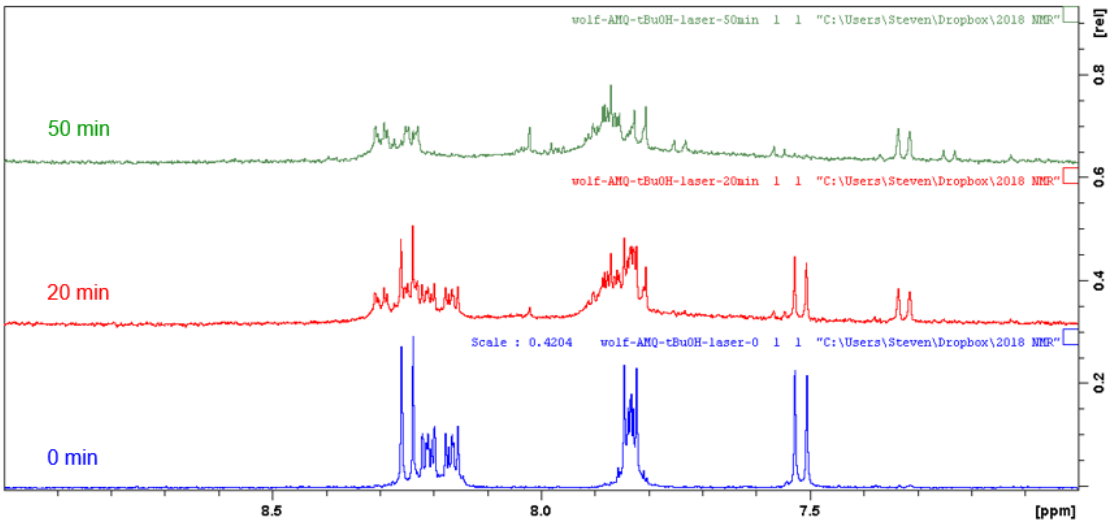


Figure 4.11 – Photolysis of **56a** in MeCN-d3 using 355 nm light monitored by ^{1}H-NMR. 355 nm light from a Nd:YAG laser operating at 10 Hz (82 mJ/pulse).

To further investigate the effects of light intensity on photolysis **56a** was dissolved in methanol (MeOH) in a four-sided quartz cuvette, sealed, purged with N_2, and photolyzed at 355nm using a Nd:YAG laser with varying power. The laser power was controlled by angle-tuning of the second harmonic. A cylindrical lens was used to increase the size of the beam to expose a larger volume of the sample. Analysis of crude photolysis mixtures were analyzed using UV-Vis absorption spectroscopy. As shown in Figure 4.12, there is a decrease in the absorption spectrum at 335 and 360 nm

corresponding to the consumption of the **56a**. There is also a significant increase in from c. 400 – c. 500 nm consistent with the formation of **55**.

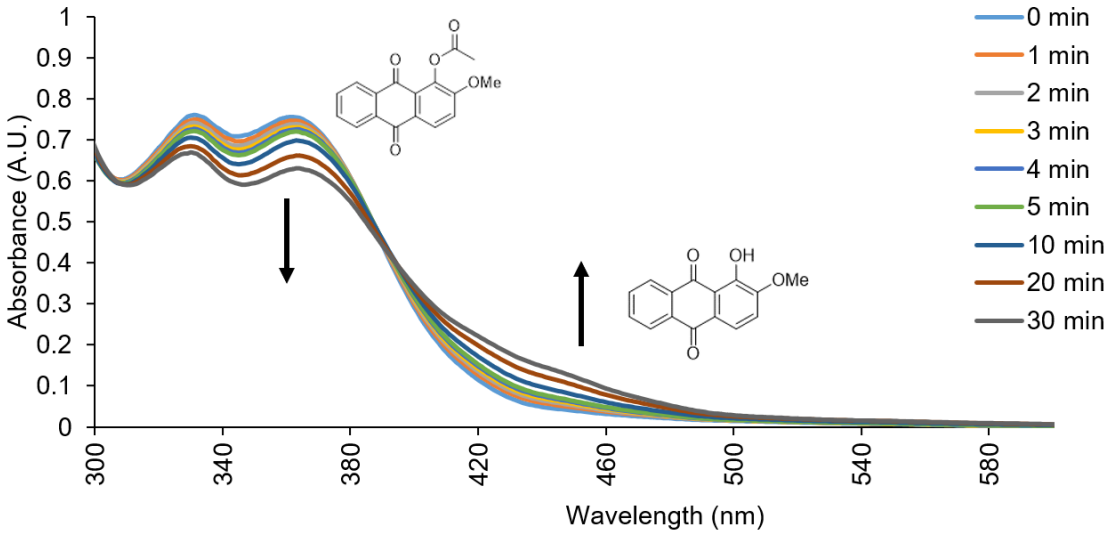


Figure 4.12 – Photolysis of **56a** in MeOH using 355 nm light from a Nd:YAG laser operating at 10 Hz monitored by UV-Vis spectroscopy.

To determine if the decomposition is a one photon process or a multiphoton process, samples of **56a** in MeOH were exposed to a set dose of 355 nm light. Though the dose was the same the varying intensities of 355 nm light were used. For each sample the formation of **53** was monitored by tracking the change in absorbance at 460 nm. Plotting the change in absorbance verses the pulse power for a one photon process will give a horizontal line as intensity is irrelevant for a given wavelength assuming a constant total energy.[28] A multiphoton process would instead give a positive slope as a greater pulse power leads to more multiphoton absorptions resulting in a greater change in absorbance. The **56a** system does result in a positive slope indicating a multiphoton process (Figure 4.13).

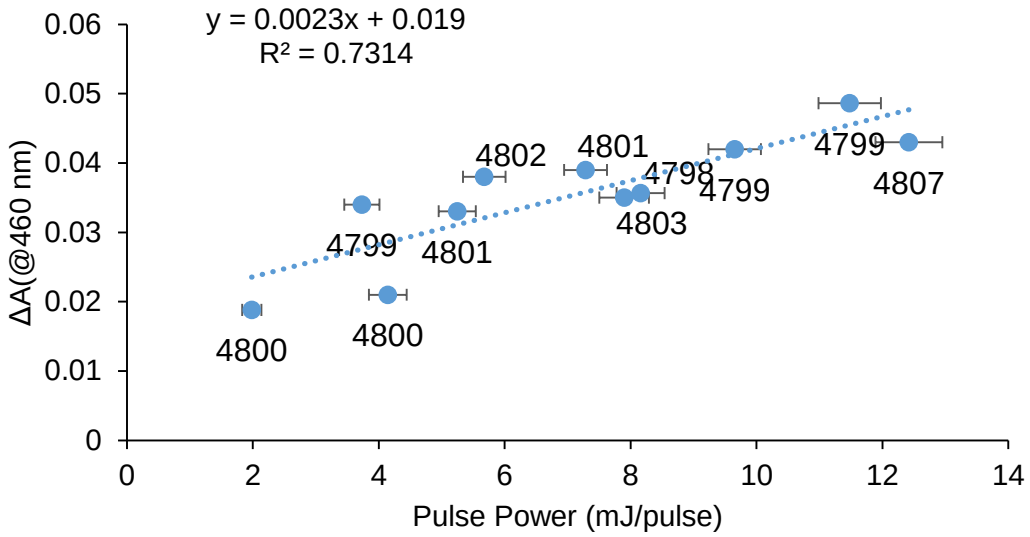


Figure 4.13 – Photolysis of **56a** in MeOH with an almost equal dose. Irradiated with 355 nm light from a Nd:YAG laser operating at 10 Hz monitored by UV-Vis spectroscopy. Numbers on the chart represent the total dose for each sample in mJ.

Table 4.2 shows the carboxylic acid production resulting from photolysis of various MAEs. Each ester produces more carboxylic acid when irradiated with 355 and 532 nm light compared to either wavelength on its own. This is consistent with the results seen in previous sections for the photolysis of **54**. It should be noted that the photolysis of MAEs is significantly slower than that of **54**, possibly due to the formation of a less active *ana* form. Future work will investigate the *ana* form further and attempt to identify a wavelength of light that can be added to 355 nm to increase *ana* formation thereby reducing carboxylic acid production.

Table 4.2 – Yield of carboxylic acid released from 40-minute photolysis of MAEs using a Nd:YAG laser operating at 10 Hz.

Compound	Solvent	%Yield 355[a]+532[b] nm	%Yield 355[a] nm	% Yield 532[b] nm
56a	Chloroform-d1	38±3	9±3	0
56b	MeCN-d3	49±7	34±11	0
56c	Chloroform-d1	57±9	36±2	0
56d	MeCN-d3	46±5	39±15	0

[a]8-12 mJ/pulse [b]87-92 mJ/pulse

4.5 Conclusions

Compound **54** and MAEs are both two-photon photoacid generators, potentially useful for photolithography and 3D nanomanufacturing. Compound **54**, in particular, releases a strong acid in excellent yields after a brief photolysis. A two-photon process makes **54** more attractive than most other sulfonate-generating photoacids due to the enhanced resolution afforded by two-photon chemistry. Future work with **54** and MAEs should focus on improving the chromophore to reduce background photolysis and potentially improve acid yields. Improved yields for carboxylic acid release could prove especially useful for drug release and other biological applications. Additionally, further investigation into the mechanism of release might provide additional insight into the design of future two- or three-photon PAGs.

Chapter 5: Supporting Information

5.1 General Methods and Materials

Chemicals and solvents were purchased from commercial suppliers and used without further purification unless otherwise stated. Acetonitrile was distilled from calcium hydride prior to use. Dichloromethane was distilled from calcium chloride prior to use. Biacetyl was distilled prior to use. Dry acetone was obtained by stirring with Drierite for several hours before it was decanted and distilled from fresh Drierite. Synthesis reactions were performed in oven dried glassware. Photolysis reactions were performed in four-sided quartz cuvettes.

2-methoxy-9,10-dioxo-9,10-dihydroanthracen-1-yl acetate (**56a**), 2-methoxy-9,10-dioxo-9,10-dihydroanthracen-1-yl 2-phenylacetate (**56b**), 2-methoxy-9,10-dioxo-9,10-dihydroanthracen-1-yl benzoate (**56c**), and 2-methoxy-9,10-dioxo-9,10-dihydroanthracen-1-yl 4-bromobenzoate (**56d**) were provided by Matthew Thum.

All NMR experiments were performed on a Bruker 400 MHz instrument. Deuterated solvents were obtained from commercial suppliers and used without further modification. All spectra are referenced to the solvent signal.

Broadband photolysis experiments were performed using a RPR-100 Rayonet photoreactor (16 bulbs, c. 400 W operating power, c. 35°C operating temperature) supplied by Southern New England Ultraviolet Company. Laser photolysis experiments were performed using a variable-power 447 nm CW diode laser supplied by Laserglow Technologies or a Nd:YAG laser (355 and 532 nm output, pulse duration 4-6 ns) supplied by Continuum.

Gas chromatography analysis was performed using a Shimadzu GC-17A containin a RTX-5 stationary phase column (length = 15 m, inner diameter (i.d.) = 0.25 mm, film thickness = 0.25 μm) and equipped with a FID detection system. The method specifications were as follows. Column temperature = 60 °C, injection temperature = 280 °C, and detector temperature = 300 °C. The temperature/pressure profile for injection was 67 kPa, 3.0 minutes, 3.9 mL/minute, 98 kPa, 9.0 minutes and for the column 60 °C, 3 minutes, 30 mL/minute, 300 °C, 9.0 minutes. Injector pressure was 60 kPa, total flow was 31 mL/min., column flow was 1.45 mL/min., and linear velocity was 39.1 cm/s.

UV-Vis data were collected on a Shimadzu UV-1800 spectrometer using UVProbe 2.43 software. Samples were scanned in the regions indicated using a fast scanning speed and a sampling interval of 1.0 nm. Each sample was pre-blanked with the solvent indicated in the experiment. FT-IR data were collected on a Thermo Nicolet 670 FT-IR with an ATR probe. Samples were performed neat using the air from the room as a blank. Mass spectra data were collected on a JEOL AccuTOF-CS using ESI-TOF or Direct Analysis in Real Time (DART).

Laser flash photolysis experiments were conducted using a Nd:YAG laser (266 and 355 nm output, pulse duration 4-6 ns) supplied by Continuum as the excitation source. The probe beam used was a 350 W Xenon arc lamp.

5.2 Chapter 2 Experimental Results and Procedures

A. General Photolysis Procedure

Photolysis experiments were carried out in four-sided quartz cuvettes sealed with rubber septa. Each solution was purged for ten minutes with nitrogen gas and the headspace of each sample was purged for five minutes with nitrogen gas. The 447 nm CW diode laser output was set to 1 W and samples were photolyzed with stirring in a temperature-controlled cuvette holder set to 20°C. The photolysis was monitored via absorption spectroscopy.

B. Synthesis of 2,2,6,6-tetramethylpiperidin-1-yl acetate (**8**)

2,2,6,6-tetramethylpiperidin-1-yl acetate was synthesized according to the procedure of Anderson and Corrie.[170] Sodium ascorbate (2.1 g, 12 mmol), sodium hydroxide (0.56 g, 14 mmol), and (2,2,6,6-Tetramethylpiperidin-1-yl)oxyl (1.0 g, 6.3 mmol) were dissolved in 18 ml of water and allowed to stir overnight. After 16 hours of stirring, the reaction flask was placed in an ice water bath and 30 ml of cold saturated sodium bicarbonate solution was added to the reaction mixture. Acetic anhydride (5.0 ml, 53 mmol) was added slowly to the reaction along with solid portions of sodium bicarbonate to maintain a basic pH. After 30 minutes, the reaction mixture was transferred to a separatory funnel and extracted three times with 10 ml portions of ethyl acetate. The organic layers were combined and rinsed once with 10 ml of saturated sodium bicarbonate solution and three times with 10 ml portions of brine. The organic layer was collected and dried with magnesium sulfate, filtered, and dried under

reduced pressure to afford a pale yellow solid. m.p.=63-65°C (lit. m.p.=63.5-65°C).

C. Radical Trapping Experiments

Experiments to trap acetyl radicals with TEMPO were monitored by gas chromatography. Samples of **8** at various concentrations in benzene were prepared, analyzed by GC, and the corresponding peak areas were measured (Table 5.1). Peak area data were used to construct a calibration curve that would be used to determine the amount of **8** produced by photolysis (Figure 5.1). Solutions for product analysis consisted of 139.2 mM TEMPO and 1.6 M **1a** in benzene. The concentration of **1a** was chosen so that its absorbance at 447 nm would be significantly greater than the absorbance of TEMPO at the same wavelength. Samples were photolyzed with a 1 W 447 nm CW diode laser for various times and injected into the GC. The peak area corresponding to **8** was measured (Table 5.2) and the calibration curve was used to determine yields of **8**.

Table 5.1 – GC peak areas for various concentrations of **8** in benzene.

[**8**] (mM)	Peak Area
167	5837595
150	5387756
133	4892240
117	4192237
99.9	3773667
83.3	3079164
66.6	2443486
50.0	1845710
33.3	1220435
16.7	594210

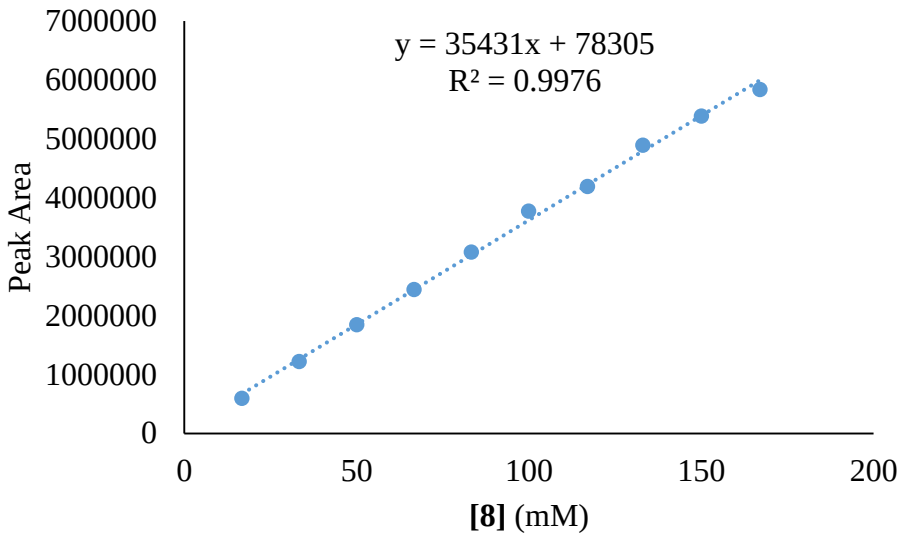


Figure 5.1 – Calibration curve for GC analysis of **8** in benzene.

Table 5.2 – Results of **1a** photolysis in benzene in the presence of TEMPO.

Photolysis Time (min)	**8** Peak Area	[**8**] (mM)
0	0	-[a]
20	185891	-[a]
40	540848	-[a]
60	1656643	44.5

[a]yields of TEMPO-Ac could not be determined due to falling below the detection limit.

D. Quenching of **1a** Decomposition

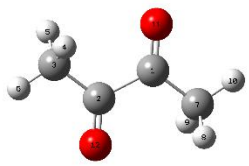
Solutions containing 0.8% v/v **1a** in benzene were photolyzed for five minutes with a 0.60 W 447 nm CW diode laser with increasing concentrations of *E*-stilbene. The decomposition of **1a** was measured using UV-Vis spectroscopy, specifically by monitoring the change in absorbance at 422 nm before and after photolysis. Table 5.3 shows the results of the quenching experiments.

Table 5.3 – Results of Quenching **1a** with *E*-stilbene.

[*E*-stiblene] (mM)	A_{422} initial (A.U.)	A_{422} final (A.U.)	ΔA	$\Delta A/\Delta A_0$
0	0.909	0.718	0.191	1
0.052	0.903	0.802	0.101	1.89
0.078	0.997	0.934	0.063	3.0
0.10	0.900	0.852	0.048	4.0
0.13	1.003	0.972	0.031	6.1
0.16	0.926	0.894	0.032	6.0
0.21	0.912	0.889	0.023	8.3
0.52	0.932	0.914	0.018	10.6

E. Chapter 2 Computational Results

Biacetyl Singlet
(U)M062x/6-311G+(d)



Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.691210	0.349726	-0.000116
2	6	0	-0.691210	-0.349726	0.000170
3	6	0	-1.892667	0.550837	0.000009
4	1	0	-1.868749	1.205153	0.874133
5	1	0	-1.868482	1.205270	-0.874018
6	1	0	-2.798930	-0.050710	-0.000160
7	6	0	1.892667	-0.550837	-0.000026
8	1	0	1.868581	-1.205191	0.874064
9	1	0	1.868650	-1.205231	-0.874087
10	1	0	2.798930	0.050710	-0.000001
11	8	0	0.738345	1.551971	0.000094
12	8	0	-0.738345	-1.551971	-0.000114

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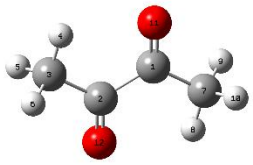
Sum of electronic and thermal Energies= -306.326413
Sum of electronic and thermal Enthalpies= -306.325469

Sum of electronic and thermal Free Energies= -306.365082

Biacetyl Triplet
(U)M062x/6-311G+(d)



Standard orientation:

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3	6	0	-1.874715	0.586718	0.000035
4	1	0	-1.531447	1.620711	-0.002162
5	1	0	-2.481870	0.382729	-0.883643
6	1	0	-2.479246	0.385830	0.886268
7	6	0	1.874812	-0.586614	0.000064
8	1	0	1.531641	-1.620622	0.001662
9	1	0	2.479738	-0.385273	-0.885785
10	1	0	2.481526	-0.382950	0.884130
11	8	0	0.778822	1.551067	-0.000043
12	8	0	-0.778922	-1.551143	0.000000

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Sum of electronic and thermal Enthalpies= -306.236044
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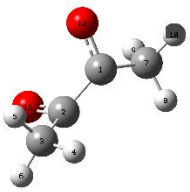
Biacetyl Quintet
(U)M062x/6-311G+(d)



Standard orientation:

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3	6	0	-0.622037	-1.840573	-0.603578
4	1	0	-0.092434	-1.907893	-1.553519
5	1	0	-0.116105	-2.479030	0.130229
6	1	0	-1.640279	-2.207326	-0.738949
7	6	0	0.622037	1.840573	-0.603578
8	1	0	0.092434	1.907893	-1.553519
9	1	0	0.116105	2.479030	0.130229
10	1	0	1.640279	2.207326	-0.738949
11	8	0	-1.484726	-0.195630	0.842894
12	8	0	1.484726	0.195630	0.842894

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Sum of electronic and thermal Energies= -306.075536
Sum of electronic and thermal Enthalpies= -306.074592
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Acyl Radical
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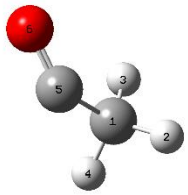

Standard orientation:

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3	1	0	1.175967	-1.190083	-0.001884
4	1	0	1.679993	0.289172	0.880505
5	6	0	-0.250112	0.432153	-0.000054
6	8	0	-1.254188	-0.174803	0.000012

Sum of electronic and zero-point Energies= -153.108642
Sum of electronic and thermal Energies= -153.104617

Sum of electronic and thermal Enthalpies= -153.103673
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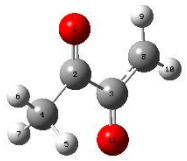
2,3-butadionyl Radical
(U)M062x/6-311G+(d)



Standard orientation:

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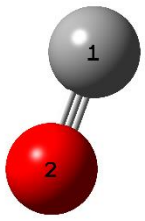
4	6	0	-1.784191	-0.673937	0.000001
5	1	0	-1.701291	-1.324730	0.873288
6	1	0	-2.739746	-0.154634	0.000402
7	1	0	-1.701748	-1.324088	-0.873817
8	6	0	1.843554	0.671644	-0.000011
9	1	0	1.659631	1.736698	0.000024
10	1	0	2.855284	0.288779	-0.000039
11	8	0	0.912358	-1.475361	0.000006

Sum of electronic and zero-point Energies= -305.689602
Sum of electronic and thermal Energies= -305.683675
Sum of electronic and thermal Enthalpies= -305.682731
Sum of electronic and thermal Free Energies= -305.719967

Carbon Monoxide
(U)M062x/6-311G+(d)



Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
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2	8	0	0.000000	0.000000	0.480912

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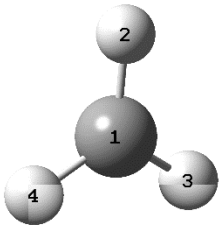
Sum of electronic and thermal Energies= -113.302357
Sum of electronic and thermal Enthalpies= -113.301413
Sum of electronic and thermal Free Energies= -113.323830

Methyl Radical
(U)M062x/6-311G+(d)



Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.000000	0.000000	0.000000
2	1	0	0.000000	1.078817	0.000000
3	1	0	0.934283	-0.539408	0.000000
4	1	0	-0.934283	-0.539408	0.000000

Sum of electronic and zero-point Energies= -39.786590
Sum of electronic and thermal Energies= -39.783490
Sum of electronic and thermal Enthalpies= -39.782546
Sum of electronic and thermal Free Energies= -39.804711

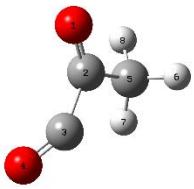
Hydrogen Atom
(U)M062x/6-311G+(d)

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	1	0	0.000000	0.000000	0.000000

Sum of electronic and zero-point Energies= -0.498134
Sum of electronic and thermal Energies= -0.496718
Sum of electronic and thermal Enthalpies= -0.495774
Sum of electronic and thermal Free Energies= -0.508788

2-oxopropanoyl Radical
(U)M062x/6-311G+(d)



Standard orientation:

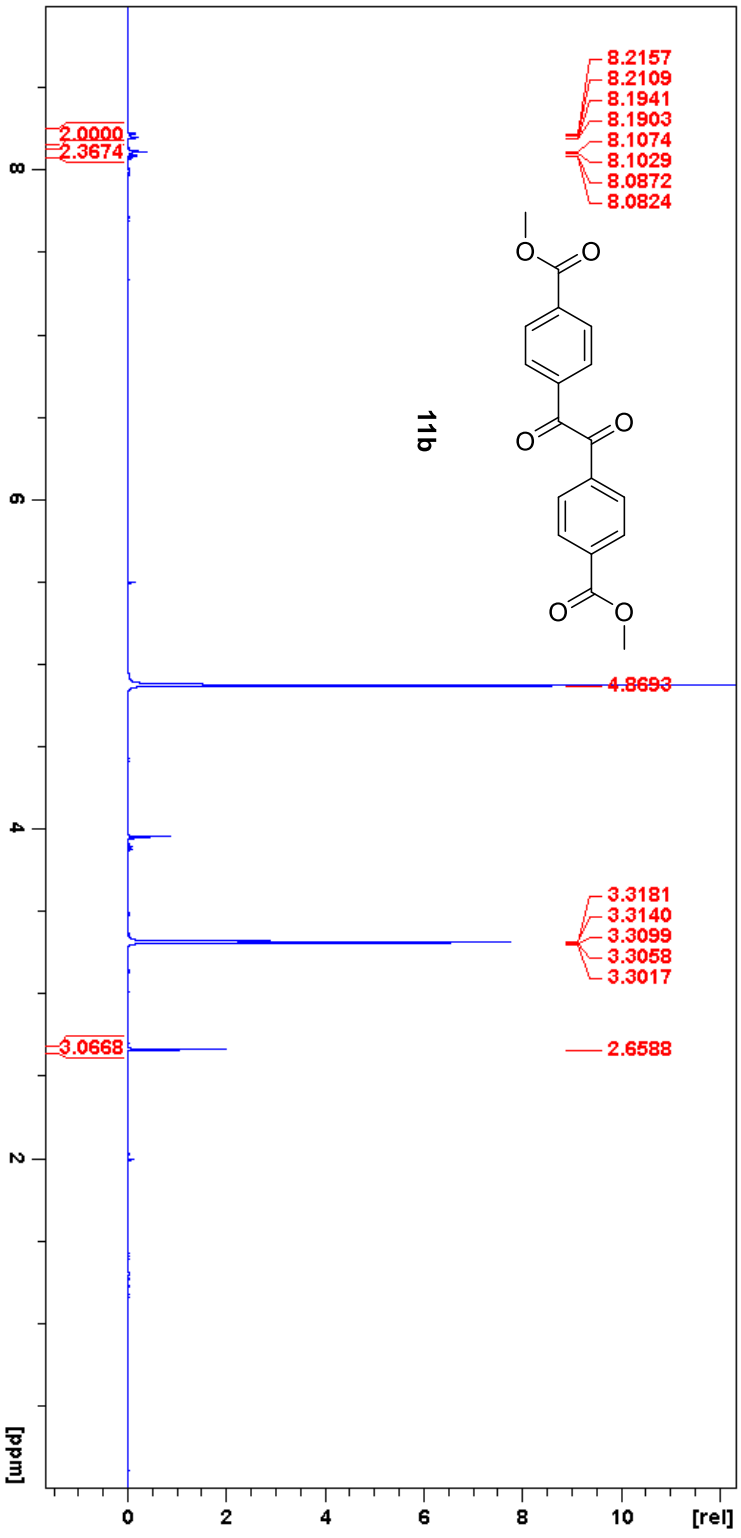
Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	8	0	0.829039	1.354694	-0.042095
2	6	0	0.448091	0.209906	0.002566
3	6	0	-0.977095	-0.080361	0.329600
4	8	0	-2.020078	-0.208777	-0.164660
5	6	0	1.333955	-1.008341	-0.036324
6	1	0	1.809443	-1.143090	0.937987
7	1	0	0.775390	-1.913250	-0.280597
8	1	0	2.113773	-0.838224	-0.778398

Sum of electronic and zero-point Energies= -266.412094
Sum of electronic and thermal Energies= -266.406271
Sum of electronic and thermal Enthalpies= -266.405327
Sum of electronic and thermal Free Energies= -266.442076

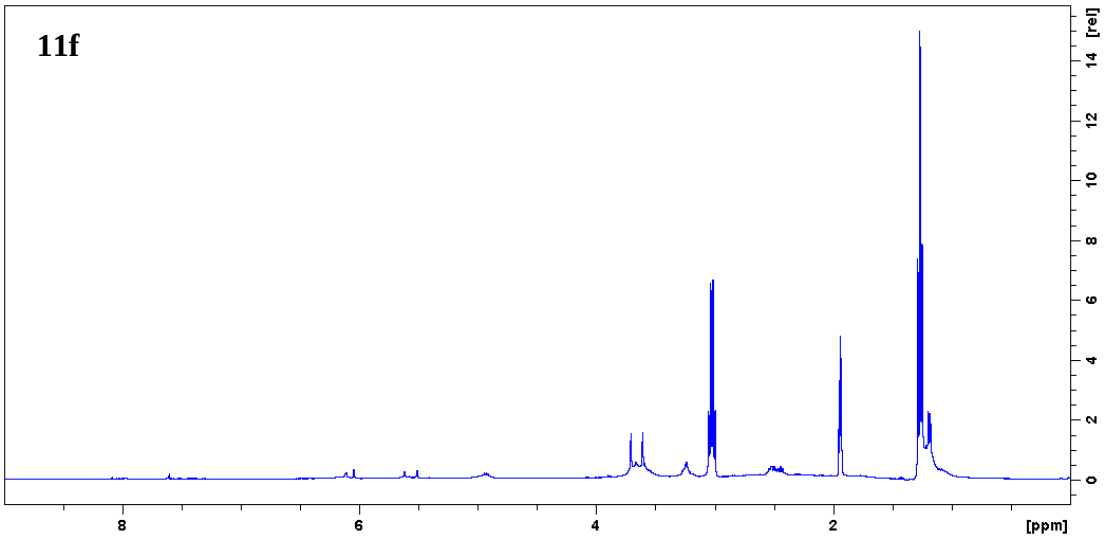
F. Synthesis of **11f**

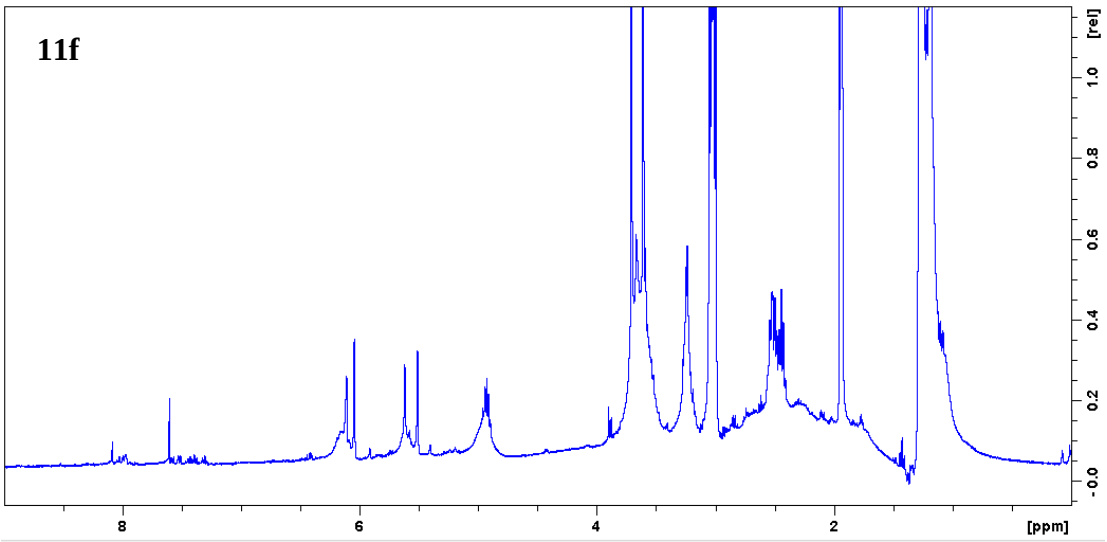
To 120 ml of acetic acid was added 1.6 g of **11b** and 55 ml of 80% sulfuric acid in water. The solution was heated to 125°C and stirred for 24h. The solution was allowed to cool to room temperature then placed in an ice water bath. To the solution was added 60 ml of water leading to the formation of precipitate. The solution was filtered to remove the solid. The solid was dissolved in 25 ml of toluene and 2.0 ml of thionyl chloride was added to the solution. The reaction was heated to reflux and stirred for 16h. After 16h of reflux, 0.7 ml of triethylamine was added to the reaction mixture followed by a solution of dipentaerythritol (0.86 g) in 35 ml of toluene. The resulting mixture was allowed to stir at room temperature for 16h then extracted with 30 ml of water. The organic layer was collected. The aqueous layer was rinsed twice with 30 ml portions of toluene. The organic layers were collected and added to the original organic layer. The combined organic layers were dried with magnesium sulfate, filtered, and the solvent removed *in vacuo*. The resulting solid was dissolved in 33 ml of triethylamine and 150 ml of toluene, to which 18 ml of acryloyl chloride was added. From this, an orange solid was collected and used as crude **11f**.

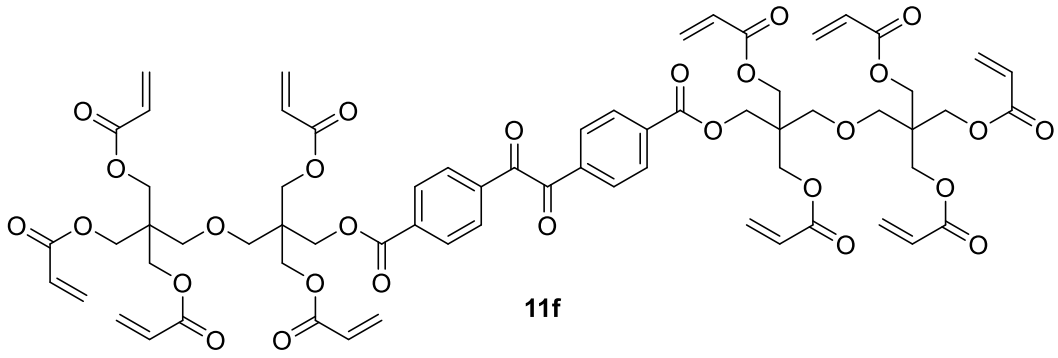
G. ^{1}H-NMR for **11a** in CD_3OD



H. ^{1}H-NMR for crude **11f** in CD_3CD.







11f

5.3 Chapter 3 Computational Results

A. Benchmarking Results for Bond Dissociation Energies

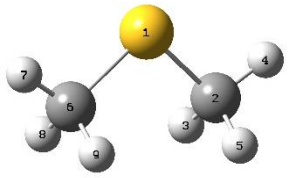
Table 5.4 – BDEs calculated using MN12SX, high level methods,[127] and experimentally determined.[129]

Molecule (Bond shown=bond broken)	Experimental	G3(MP2)-RAD	(U)MN12SX/6-311G++(d,p)// (U)MN12SX/6-31G(d)
HS-H	91.10±0.01	90.7	91.3
CH3S-H	87.4±0.5	86.4	86.2
CH3CH2S-H	87.3	86.1	85.6
(CH3)2CHS-H	88.4±2	87.5	87.1
(CH3)3CS-H	86.6±2.2	87.7	87.3
C6H5C(S)S-H	87.9	75.6	73.3
HSS-H	76±3.5	73.8	73.2
CH3SS-H	79±3.5 70.5	70.9	65.2
CH2=CHS-H	84±2	87.8	86.9
C6H5S-H	83.5±1.1	80.2	77.8
CH3C(O)S-H	87	88	87
NH2CH(COOH)CH2S-H		88	85.5
C6H5CH2S-H	86.9 87.8	88.6	86.1
C6H5S-H	83.5±1.1	80.2	77.8
*p*Cl-C6H4S-H	79.2 79.9 86.1±0.8	79.9	77.2
*p*CH3-C6H4S-H	78.3 77.8 78.4 80.0 84.8±1.0	79.3	76.8
*p*CH3O-C6H4S-H	76.9 76.2 78.6 78.7 83.3±1.0	77.8	75.3
*p*NO2-C6H4S-H	81.4 81.6	82.9	83.3
*p*NH2-C6H4S-H	69.8 70.0	76.9	73.5
HS-CH3	74.7±1	73.1	75.6

CH3S-CH3	73.6±0.8	71	73.6
CH3CH2S-CH3	73.4±1.5	71.5	72.9
HSS-CH3	57±1.5	61.1	56.5
CH3SS-CH3	56.6 57.4±1.5	58	59.3
C6H5S-CH3	66.5±2.5	66.3	64.9
HS-SH	64.7±1	62.2	61.3
CH3S-SCH3	65.2±0.9	63	59.8
CH3CH2S-SCH2CH3	66.1	64.4	58.9
HSS-SSH	33.6±2	41.6	36.5
CH3SS-SSCH3	32.9	37.4	32.7
C6H5S-SC6H5	51.2±3	52.8	44.5
CH3-Cl	70±3	65.4	62.9
CH3SS-Cl	51±2.5	53.5	50.2
C6H5S-Cl	31±2.5	58.6	54.4

B. Ground State Calculations for Chapter 3

Dimethyl Sulfande
(U)CAM-B3LYP/6-311G++(d,p)

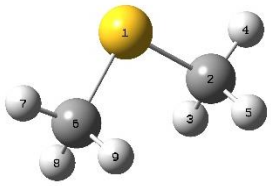


Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	16	0	0.000000	0.659390	0.000000
2	6	0	1.380298	-0.511604	0.000000
3	1	0	1.364521	-1.138875	-0.892202
4	1	0	2.300078	0.072273	0.000013
5	1	0	1.364506	-1.138894	0.892188
6	6	0	-1.380298	-0.511604	0.000000
7	1	0	-2.300078	0.072273	-0.000027
8	1	0	-1.364497	-1.138900	-0.892183
9	1	0	-1.364529	-1.138869	0.892207

Sum of electronic and zero-point Energies= -477.925580
Sum of electronic and thermal Energies= -477.920713
Sum of electronic and thermal Enthalpies= -477.919769
Sum of electronic and thermal Free Energies= -477.952608

Dimethyl Sulfane
(U)B3LYP/6-311G++(d,p)

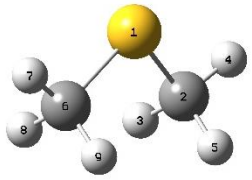


Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	16	0	0.000000	0.000000	0.661841
2	6	0	0.000000	1.394183	-0.514809
3	1	0	-0.893911	1.380590	-1.141747
4	1	0	0.000000	2.309868	0.077623
5	1	0	0.893911	1.380590	-1.141747
6	6	0	0.000000	-1.394183	-0.514809
7	1	0	0.000000	-2.309868	0.077623
8	1	0	-0.893911	-1.380590	-1.141747
9	1	0	0.893911	-1.380590	-1.141747

Sum of electronic and zero-point Energies= -477.991542
Sum of electronic and thermal Energies= -477.986619
Sum of electronic and thermal Enthalpies= -477.985675
Sum of electronic and thermal Free Energies= -478.017981

Dimethyl Sulfane
(U)MN12SX/6-311G++(d,p)



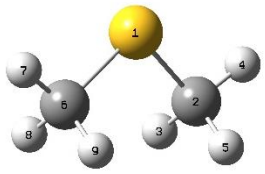
Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	16	0	0.000000	0.000000	0.664373
2	6	0	0.000000	1.361637	-0.513055
3	1	0	-0.894885	1.340628	-1.146689
4	1	0	0.000000	2.295678	0.056723
5	1	0	0.894885	1.340628	-1.146689

6	6	0	0.000000	-1.361637	-0.513055
7	1	0	0.000000	-2.295678	0.056723
8	1	0	-0.894885	-1.340628	-1.146689
9	1	0	0.894885	-1.340628	-1.146689

Sum of electronic and zero-point Energies= -477.841203
Sum of electronic and thermal Energies= -477.836313
Sum of electronic and thermal Enthalpies= -477.835369
Sum of electronic and thermal Free Energies= -477.867602

Dimethyl Sulfane
(U)PBE0/6-311G++(d,p)

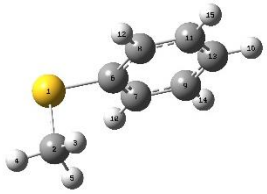


Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	16	0	0.000000	0.663233	0.000000
2	6	0	1.391058	-0.515354	0.000000
3	1	0	1.379146	-1.147323	-0.900676
4	1	0	2.313742	0.080907	-0.000003
5	1	0	1.379150	-1.147319	0.900679
6	6	0	-1.391058	-0.515354	0.000000
7	1	0	-2.313742	0.080907	-0.000003
8	1	0	-1.379147	-1.147322	-0.900676
9	1	0	-1.379150	-1.147319	0.900679

Sum of electronic and zero-point Energies= -477.679315
Sum of electronic and thermal Energies= -477.674335
Sum of electronic and thermal Enthalpies= -477.673391
Sum of electronic and thermal Free Energies= -477.706453

Methyl(phenyl)sulfane
(U)CAM-B3LYP/6-311G++(d,p)

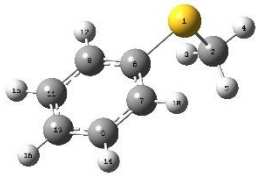


Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	16	0	-1.879929	-0.001703	-0.630622
2	6	0	-2.546009	0.002369	1.062216
3	1	0	-2.234368	0.895860	1.601774
4	1	0	-3.632565	0.002090	0.971682
5	1	0	-2.234235	-0.888421	1.606146
6	6	0	-0.126212	-0.000674	-0.276084
7	6	0	0.564332	-1.203130	-0.150732
8	6	0	0.563435	1.202500	-0.152876
9	6	0	1.928242	-1.201122	0.107568
10	1	0	0.028465	-2.137726	-0.263242
11	6	0	1.927352	1.201956	0.105482
12	1	0	0.026954	2.136531	-0.267158
13	6	0	2.610998	0.000795	0.238170
14	1	0	2.458673	-2.141158	0.202568
15	1	0	2.457057	2.142568	0.198827
16	1	0	3.676051	0.001346	0.436883

Sum of electronic and zero-point Energies= -669.543038
Sum of electronic and thermal Energies= -669.535304
Sum of electronic and thermal Enthalpies= -669.534360
Sum of electronic and thermal Free Energies= -669.577228

Methyl(phenyl)sulfane
(U)B3LYP/6-311G++(d,p)



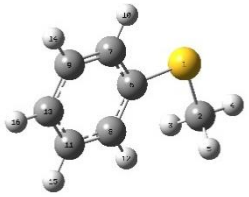
Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	16	0	-1.885056	-0.113329	-0.627382
2	6	0	-2.580227	0.156790	1.049523
3	1	0	-2.280992	1.128030	1.444017
4	1	0	-3.665294	0.133772	0.938238
5	1	0	-2.271219	-0.636803	1.730029
6	6	0	-0.123075	-0.044369	-0.267697
7	6	0	0.599760	-1.225883	-0.076096

8	6	0	0.541079	1.185643	-0.217022
9	6	0	1.970627	-1.175848	0.173956
10	1	0	0.086046	-2.178576	-0.128261
11	6	0	1.910299	1.232179	0.038585
12	1	0	-0.015507	2.100040	-0.386406
13	6	0	2.626983	0.052185	0.234745
14	1	0	2.524226	-2.096830	0.319457
15	1	0	2.417953	2.189654	0.076338
16	1	0	3.693011	0.089786	0.428738

Sum of electronic and zero-point Energies= -669.719204
Sum of electronic and thermal Energies= -669.711368
Sum of electronic and thermal Enthalpies= -669.710424
Sum of electronic and thermal Free Energies= -669.752994

Methyl(phenyl)sulfane
(U)MN12SX/6-311G++(d,p)



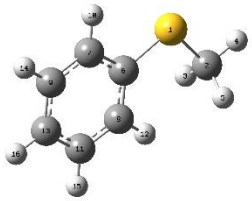
Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	16	0	1.816358	0.716208	-0.000588
2	6	0	2.679911	-0.859088	0.000984
3	1	0	2.458807	-1.447288	-0.896492
4	1	0	3.746468	-0.615466	0.001619
5	1	0	2.457420	-1.446104	0.898892
6	6	0	0.119884	0.232640	-0.000223
7	6	0	-0.826278	1.265041	0.000262
8	6	0	-0.322402	-1.090543	-0.000505
9	6	0	-2.180703	0.975253	0.000444
10	1	0	-0.490386	2.300990	0.000555
11	6	0	-1.685718	-1.369520	-0.000290
12	1	0	0.383450	-1.915548	-0.000929
13	6	0	-2.621107	-0.345345	0.000177
14	1	0	-2.900695	1.791542	0.000843
15	1	0	-2.013393	-2.407704	-0.000518
16	1	0	-3.684928	-0.570380	0.000345

Sum of electronic and zero-point Energies= -669.422338

Sum of electronic and thermal Energies= -669.414776
Sum of electronic and thermal Enthalpies= -669.413832
Sum of electronic and thermal Free Energies= -669.455373

Methyl(phenyl)sulfane
(U)PBE0/6-311G++(d,p)

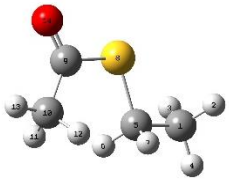


Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	16	0	-1.827133	-0.721128	0.000003
2	6	0	-2.719851	0.863454	-0.000005
3	1	0	-2.503059	1.451332	-0.903203
4	1	0	-3.785071	0.595472	-0.000010
5	1	0	-2.503068	1.451336	0.903193
6	6	0	-0.115671	-0.232284	0.000002
7	6	0	0.834668	-1.273900	-0.000001
8	6	0	0.329532	1.100754	0.000003
9	6	0	2.199177	-0.981834	-0.000002
10	1	0	0.497934	-2.314032	-0.000002
11	6	0	1.702324	1.381160	0.000001
12	1	0	-0.382094	1.927388	0.000005
13	6	0	2.643762	0.347969	-0.000001
14	1	0	2.921520	-1.801921	-0.000005
15	1	0	2.032093	2.423281	0.000002
16	1	0	3.712226	0.573264	-0.000003

Sum of electronic and zero-point Energies= -669.169791
Sum of electronic and thermal Energies= -669.161947
Sum of electronic and thermal Enthalpies= -669.161003
Sum of electronic and thermal Free Energies= -669.202825

S-ethyl thioacetate
(U)CAM-B3LYP/6-311G++(d,p)

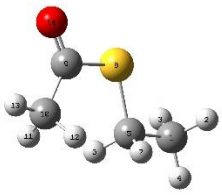


Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	2.822870	0.045941	0.000002
2	1	0	3.012179	-0.565971	-0.883560
3	1	0	3.012153	-0.565720	0.883744
4	1	0	3.539053	0.869953	-0.000105
5	6	0	1.402393	0.594276	-0.000097
6	1	0	1.234891	1.207301	0.885364
7	1	0	1.234921	1.207058	-0.885732
8	16	0	0.231294	-0.810112	0.000077
9	6	0	-1.402103	-0.074784	0.000012
10	6	0	-1.533082	1.426627	-0.000128
11	1	0	-1.056255	1.857694	0.881823
12	1	0	-1.056089	1.857566	-0.882049
13	1	0	-2.592817	1.674651	-0.000239
14	8	0	-2.346152	-0.816638	0.000097

Sum of electronic and zero-point Energies= -630.512538
Sum of electronic and thermal Energies= -630.504591
Sum of electronic and thermal Enthalpies= -630.503647
Sum of electronic and thermal Free Energies= -630.545473

S-ethyl thioacetate
(U)B3LYP/6-311G++(d,p)

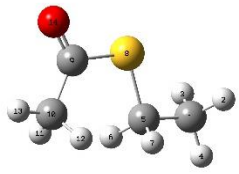


Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	2.847126	0.044468	0.000049
2	1	0	3.036661	-0.567627	-0.884666
3	1	0	3.036542	-0.567178	0.885099
4	1	0	3.564377	0.869761	-0.000112
5	6	0	1.423013	0.598691	-0.000189
6	1	0	1.253447	1.211015	0.886785
7	1	0	1.253577	1.210582	-0.887486
8	16	0	0.232473	-0.811838	0.000081
9	6	0	-1.418617	-0.074623	-0.000045
10	6	0	-1.551713	1.432945	-0.000035
11	1	0	-1.074724	1.865610	0.882784
12	1	0	-1.074440	1.865667	-0.882667
13	1	0	-2.612495	1.682001	-0.000186
14	8	0	-2.362672	-0.823665	0.000058

Sum of electronic and zero-point Energies= -630.646973
Sum of electronic and thermal Energies= -630.638911
Sum of electronic and thermal Enthalpies= -630.637967
Sum of electronic and thermal Free Energies= -630.680035

S-ethyl thioacetate
(U)MN12SX/6-311G++(d,p)



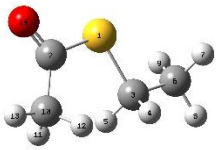
Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	2.804869	0.046344	0.000024

2	1	0	2.995257	-0.569074	-0.886081
3	1	0	2.995187	-0.568780	0.886349
4	1	0	3.525564	0.871287	-0.000086
5	6	0	1.386274	0.590614	-0.000122
6	1	0	1.216545	1.209930	0.889080
7	1	0	1.216624	1.209653	-0.889532
8	16	0	0.230456	-0.816370	0.000045
9	6	0	-1.394206	-0.074809	0.000022
10	6	0	-1.505681	1.428318	-0.000099
11	1	0	-1.019330	1.855643	0.883582
12	1	0	-1.019119	1.855551	-0.883706
13	1	0	-2.565084	1.694626	-0.000228
14	8	0	-2.347560	-0.804965	0.000119

Sum of electronic and zero-point Energies= -630.376758
Sum of electronic and thermal Energies= -630.368859
Sum of electronic and thermal Enthalpies= -630.367915
Sum of electronic and thermal Free Energies= -630.409650

S-ethyl thioacetate
(U)PBE0/6-311G++(d,p)

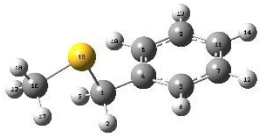


Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	16	0	0.231722	-0.811154	-0.000002
2	6	0	-1.422500	-0.071624	0.000001
3	6	0	1.425649	0.596795	0.000009
4	1	0	1.253570	1.214219	-0.894023
5	1	0	1.253576	1.214195	0.894058
6	6	0	2.848245	0.037907	-0.000004
7	1	0	3.037676	-0.579333	-0.890811
8	1	0	3.574729	0.865463	0.000007
9	1	0	3.037681	-0.579360	0.890784
10	6	0	-1.540685	1.437496	-0.000004
11	1	0	-1.054570	1.870495	0.887885
12	1	0	-1.054572	1.870487	-0.887898
13	1	0	-2.606055	1.701116	-0.000003
14	8	0	-2.376729	-0.825284	0.000003

Sum of electronic and zero-point Energies= -630.164858
Sum of electronic and thermal Energies= -630.156655
Sum of electronic and thermal Enthalpies= -630.155711
Sum of electronic and thermal Free Energies= -630.198104

Benzyl(methyl)sulfane
(U)CAM-B3LYP/6-311G++(d,p)

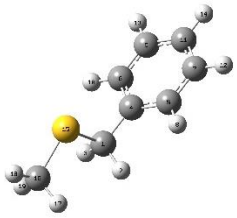


Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-1.010628	0.000673	0.813511
2	1	0	-1.249663	0.886515	1.404803
3	1	0	-1.249748	-0.884286	1.406097
4	6	0	0.441424	0.000326	0.428523
5	6	0	1.124826	1.198470	0.238122
6	6	0	1.124390	-1.198159	0.238695
7	6	0	2.463529	1.200043	-0.126464
8	1	0	0.601059	2.138069	0.375986
9	6	0	2.463087	-1.200392	-0.125908
10	1	0	0.600280	-2.137503	0.376994
11	6	0	3.136815	-0.000341	-0.308627
12	1	0	2.982418	2.140811	-0.267225
13	1	0	2.981624	-2.141419	-0.266229
14	1	0	4.182599	-0.000593	-0.591718
15	16	0	-2.066237	-0.000388	-0.680747
16	6	0	-3.691429	0.000073	0.119387
17	1	0	-3.830526	0.892725	0.730475
18	1	0	-4.439896	-0.000485	-0.672319
19	1	0	-3.830447	-0.891779	0.731660

Sum of electronic and zero-point Energies= -708.815199
Sum of electronic and thermal Energies= -708.806150
Sum of electronic and thermal Enthalpies= -708.805206
Sum of electronic and thermal Free Energies= -708.851038

Benzyl(methyl)sulfane
(U)B3LYP/6-311G++(d,p)

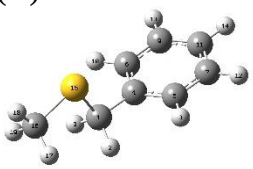


Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-1.007756	0.000695	0.821134
2	1	0	-1.249517	0.888185	1.410858
3	1	0	-1.249601	-0.885894	1.412185
4	6	0	0.445984	0.000338	0.430900
5	6	0	1.133424	1.203587	0.238747
6	6	0	1.132978	-1.203269	0.239338
7	6	0	2.477321	1.204920	-0.127950
8	1	0	0.610561	2.144371	0.377053
9	6	0	2.476863	-1.205282	-0.127373
10	1	0	0.609760	-2.143789	0.378096
11	6	0	3.153424	-0.000350	-0.311429
12	1	0	2.996501	2.146450	-0.268651
13	1	0	2.995689	-2.147075	-0.267625
14	1	0	4.199816	-0.000612	-0.595212
15	16	0	-2.080509	-0.000400	-0.684107
16	6	0	-3.719504	0.000076	0.121579
17	1	0	-3.859085	0.894456	0.732100
18	1	0	-4.463366	-0.000484	-0.676056
19	1	0	-3.859017	-0.893499	0.733295

Sum of electronic and zero-point Energies= -709.017004
Sum of electronic and thermal Energies= -709.007827
Sum of electronic and thermal Enthalpies= -709.006883
Sum of electronic and thermal Free Energies= -709.052881

Benzyl(methyl)sulfane
(U)MN12SX/6-311G++(d,p)



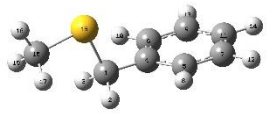
Standard orientation:

Center	Atomic	Atomic	Coordinates (Angstroms)

Number	Number	Type	X	Y	Z
1	6	0	-1.019283	0.000600	0.814601
2	1	0	-1.266561	0.891118	1.408756
3	1	0	-1.266686	-0.889321	1.409604
4	6	0	0.432870	0.000301	0.439142
5	6	0	1.114768	1.200880	0.243692
6	6	0	1.114287	-1.200619	0.244071
7	6	0	2.453223	1.202104	-0.126643
8	1	0	0.585358	2.143059	0.383290
9	6	0	2.452734	-1.202515	-0.126254
10	1	0	0.584478	-2.142532	0.383954
11	6	0	3.125903	-0.000368	-0.312003
12	1	0	2.974505	2.146511	-0.270778
13	1	0	2.973634	-2.147179	-0.270086
14	1	0	4.175060	-0.000623	-0.600786
15	16	0	-2.050346	-0.000097	-0.687120
16	6	0	-3.662630	-0.000187	0.115339
17	1	0	-3.800334	0.894888	0.733524
18	1	0	-4.425185	-0.000560	-0.669249
19	1	0	-3.799970	-0.894975	0.734024

Sum of electronic and zero-point Energies= -708.677809
Sum of electronic and thermal Energies= -708.668717
Sum of electronic and thermal Enthalpies= -708.667772
Sum of electronic and thermal Free Energies= -708.713448

Benzyl(methyl)sulfane
(U)PBE0/6-311G++(d,p)



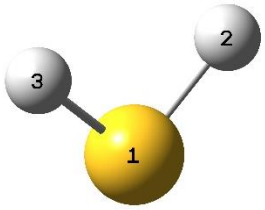
Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-1.013383	-0.000063	0.829279
2	1	0	-1.258928	0.895197	1.422370
3	1	0	-1.258921	-0.895402	1.422251
4	6	0	0.440281	-0.000031	0.437869
5	6	0	1.128954	1.209192	0.242204
6	6	0	1.128995	-1.209221	0.242151
7	6	0	2.477541	1.210700	-0.129349
8	1	0	0.599755	2.156072	0.382856

9	6	0	2.477582	-1.210667	-0.129402
10	1	0	0.599828	-2.156125	0.382762
11	6	0	3.156009	0.000032	-0.315365
12	1	0	3.000569	2.159461	-0.272332
13	1	0	3.000643	-2.159404	-0.272425
14	1	0	4.209986	0.000056	-0.603374
15	16	0	-2.074171	0.000036	-0.684659
16	6	0	-3.716056	-0.000006	0.111926
17	1	0	-3.862788	0.900716	0.726521
18	1	0	-4.460157	0.000044	-0.696362
19	1	0	-3.862793	-0.900801	0.726414

Sum of electronic and zero-point Energies= -708.408413
Sum of electronic and thermal Energies= -708.399002
Sum of electronic and thermal Enthalpies= -708.398057
Sum of electronic and thermal Free Energies= -708.444632

Hydrogen Sulfide
(U)CAM-B3LYP/6-311G++(d,p)

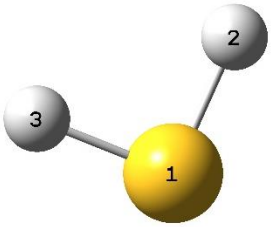


Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	16	0	0.000000	0.000000	0.103026
2	1	0	0.000000	0.972114	-0.824208
3	1	0	0.000000	-0.972114	-0.824208

Sum of electronic and zero-point Energies= -399.394722
Sum of electronic and thermal Energies= -399.391874
Sum of electronic and thermal Enthalpies= -399.390930
Sum of electronic and thermal Free Energies= -399.414278

Hydrogen Sulfide
(U)B3LYP/6-311G++(d,p)

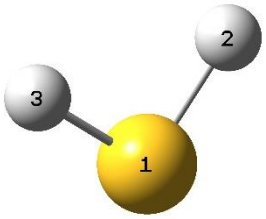


Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	16	0	0.000000	0.000000	0.103568
2	1	0	0.000000	0.973196	-0.828547
3	1	0	0.000000	-0.973196	-0.828547

Sum of electronic and zero-point Energies= -399.407646
Sum of electronic and thermal Energies= -399.404797
Sum of electronic and thermal Enthalpies= -399.403852
Sum of electronic and thermal Free Energies= -399.427210

Hydrogen Sulfide
(U)MN12SX/6-311G++(d,p)

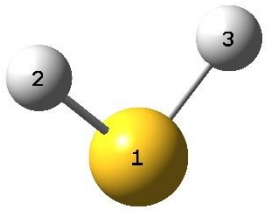


Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	16	0	0.000000	0.000000	0.103513
2	1	0	0.000000	0.967325	-0.828105
3	1	0	0.000000	-0.967325	-0.828105

Sum of electronic and zero-point Energies= -399.340839
Sum of electronic and thermal Energies= -399.337990
Sum of electronic and thermal Enthalpies= -399.337046
Sum of electronic and thermal Free Energies= -399.360394

Hydrogen Sulfide
(U)PBE0/6-311G++(d,p)

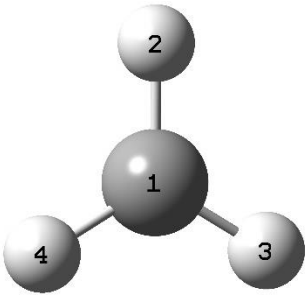


Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	16	0	0.000000	0.000000	0.105027
2	1	0	0.000000	-0.974205	-0.840216
3	1	0	0.000000	0.974205	-0.840216

Sum of electronic and zero-point Energies= -399.209202
Sum of electronic and thermal Energies= -399.206349
Sum of electronic and thermal Enthalpies= -399.205405
Sum of electronic and thermal Free Energies= -399.228788

Methyl Radical
(U)CAM-B3LYP/6-311G++(d,p)

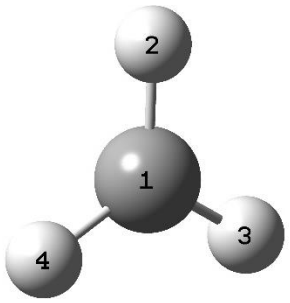


Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.000000	0.000000	0.000431
2	1	0	0.000000	1.080123	-0.000862
3	1	0	0.935414	-0.540061	-0.000862
4	1	0	-0.935414	-0.540061	-0.000862

Sum of electronic and zero-point Energies= -39.793860
Sum of electronic and thermal Energies= -39.790823
Sum of electronic and thermal Enthalpies= -39.789879
Sum of electronic and thermal Free Energies= -39.812599

Methyl Radical
(U)B3LYP/6-311G++(d,p)

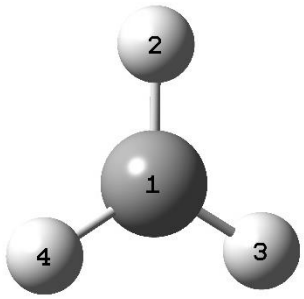


Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.000000	0.000000	0.000018
2	1	0	0.000000	1.080653	-0.000037
3	1	0	0.935873	-0.540326	-0.000037
4	1	0	-0.935873	-0.540326	-0.000037

Sum of electronic and zero-point Energies= -39.825549
Sum of electronic and thermal Energies= -39.822504
Sum of electronic and thermal Enthalpies= -39.821560
Sum of electronic and thermal Free Energies= -39.844295

Methyl Radical
(U)MN12SX/6-311G++(d,p)

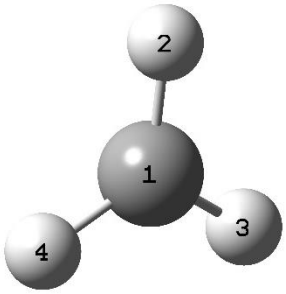


Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.000000	0.000000	-0.000337
2	1	0	0.000000	1.082635	0.000675
3	1	0	0.937589	-0.541317	0.000675
4	1	0	-0.937589	-0.541317	0.000675

Sum of electronic and zero-point Energies= -39.769197
Sum of electronic and thermal Energies= -39.765995
Sum of electronic and thermal Enthalpies= -39.765051
Sum of electronic and thermal Free Energies= -39.788060

Methyl Radical
(U)PBE0/6-311G++(d,p)

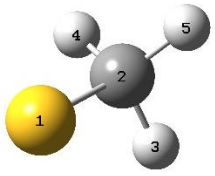


Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.000000	0.000000	0.000000
2	1	0	0.000000	1.088439	-0.000001
3	1	0	0.942616	-0.544220	-0.000001
4	1	0	-0.942616	-0.544220	-0.000001

Sum of electronic and zero-point Energies= -39.755757
Sum of electronic and thermal Energies= -39.752703
Sum of electronic and thermal Enthalpies= -39.751758
Sum of electronic and thermal Free Energies= -39.774526

Methanethiyl Radical
(U)CAM-B3LYP/6-311G++(d,p)



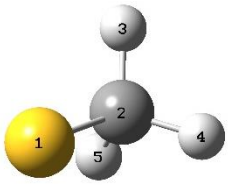
Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	16	0	0.691868	0.000007	-0.001841
2	6	0	-1.106006	0.000044	-0.008332
3	1	0	-1.423634	-0.002389	1.039130

4	1	0	-1.505202	0.898016	-0.477918
5	1	0	-1.505018	-0.896008	-0.481763

Sum of electronic and zero-point Energies= -438.028563
Sum of electronic and thermal Energies= -438.025380
Sum of electronic and thermal Enthalpies= -438.024436
Sum of electronic and thermal Free Energies= -438.052830

Methanethiyl Radical
(U)B3LYP/6-311G++(d,p)

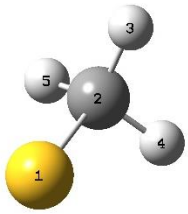


Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	16	0	-0.696038	-0.000050	-0.001873
2	6	0	1.113291	-0.000157	-0.008651
3	1	0	1.512891	0.893127	-0.490170
4	1	0	1.429907	0.012943	1.041235
5	1	0	1.514061	-0.904334	-0.469183

Sum of electronic and zero-point Energies= -438.065116
Sum of electronic and thermal Energies= -438.061912
Sum of electronic and thermal Enthalpies= -438.060968
Sum of electronic and thermal Free Energies= -438.089405

Methanethiyl Radical
(U)MN12SX/6-311G++(d,p)



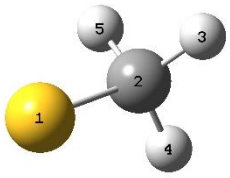
Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	16	0	0.000000	0.000000	0.661841

2	6	0	0.000000	1.394183	-0.514809
3	1	0	-0.893911	1.380590	-1.141747
4	1	0	0.000000	2.309868	0.077623
5	1	0	0.893911	1.380590	-1.141747
6	6	0	0.000000	-1.394183	-0.514809
7	1	0	0.000000	-2.309868	0.077623
8	1	0	-0.893911	-1.380590	-1.141747
9	1	0	0.893911	-1.380590	-1.141747

Sum of electronic and zero-point Energies= -477.991542
Sum of electronic and thermal Energies= -477.986619
Sum of electronic and thermal Enthalpies= -477.985675
Sum of electronic and thermal Free Energies= -478.017981

Methanethiyl Radical
(U)PBE0/6-311G++(d,p)

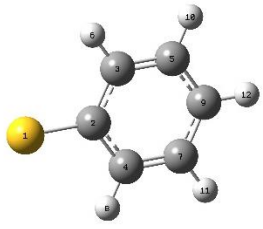


Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	16	0	-0.694609	0.000002	0.002070
2	6	0	1.108381	0.000011	0.010444
3	1	0	1.519325	0.907072	0.476356
4	1	0	1.519261	-0.906685	0.477126
5	1	0	1.424863	-0.000490	-1.049270

Sum of electronic and zero-point Energies= -437.812487
Sum of electronic and thermal Energies= -437.809253
Sum of electronic and thermal Enthalpies= -437.808309
Sum of electronic and thermal Free Energies= -437.836790

Phenylthiyl Radical
(U)CAM-B3LYP/6-311G++(d,p)

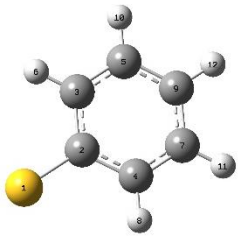


Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	16	0	-2.292815	0.000000	-0.000002
2	6	0	-0.571937	-0.000005	0.000017
3	6	0	0.148166	1.212249	-0.000019
4	6	0	0.148157	-1.212242	0.000014
5	6	0	1.529547	1.207560	0.000018
6	1	0	-0.403893	2.143161	-0.000033
7	6	0	1.529557	-1.207553	-0.000015
8	1	0	-0.403869	-2.143173	-0.000007
9	6	0	2.223216	-0.000007	0.000002
10	1	0	2.073037	2.144441	0.000002
11	1	0	2.073019	-2.144450	-0.000021
12	1	0	3.306511	0.000011	-0.000008

Sum of electronic and zero-point Energies= -629.657146
Sum of electronic and thermal Energies= -629.651643
Sum of electronic and thermal Enthalpies= -629.650699
Sum of electronic and thermal Free Energies= -629.687563

Phenylthiyl Radical
(U)B3LYP/6-311G++(d,p)

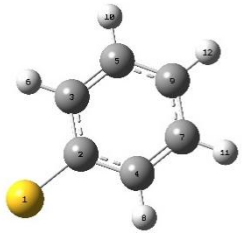


Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	16	0	-2.303730	0.000000	-0.000016
2	6	0	-0.575983	-0.000021	0.000090
3	6	0	0.150220	-1.218008	-0.000036
4	6	0	0.150190	1.217990	-0.000025
5	6	0	1.536274	-1.212732	-0.000003
6	1	0	-0.401574	-2.149965	0.000107
7	6	0	1.536249	1.212750	-0.000034
8	1	0	-0.401644	2.149922	0.000110
9	6	0	2.233675	0.000017	-0.000011
10	1	0	2.080680	-2.150224	0.000045
11	1	0	2.080641	2.150249	0.000108
12	1	0	3.317812	0.000037	0.000003

Sum of electronic and zero-point Energies= -629.805586
Sum of electronic and thermal Energies= -629.800005
Sum of electronic and thermal Enthalpies= -629.799061
Sum of electronic and thermal Free Energies= -629.836072

Phenylthiyl Radical
(U)MN12SX/6-311G++(d,p)



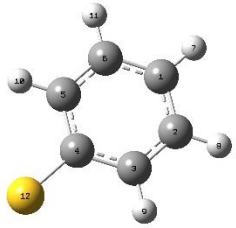
Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	16	0	0.000000	2.290786	0.000000

2	6	0	0.000000	0.578002	0.000000
3	6	0	0.000000	-0.147588	1.215165
4	6	0	0.000000	-0.147588	-1.215165
5	6	0	0.000000	-1.529519	1.209681
6	1	0	0.000000	0.408772	2.150472
7	6	0	0.000000	-1.529519	-1.209681
8	1	0	0.000000	0.408772	-2.150472
9	6	0	0.000000	-2.224344	0.000000
10	1	0	0.000000	-2.076849	2.150592
11	1	0	0.000000	-2.076849	-2.150592
12	1	0	0.000000	-3.313079	0.000000

Sum of electronic and zero-point Energies= -629.549818
Sum of electronic and thermal Energies= -629.544249
Sum of electronic and thermal Enthalpies= -629.543305
Sum of electronic and thermal Free Energies= -629.580285

Phenylthiyl Radical
(U)PBE0/6-311G++(d,p)



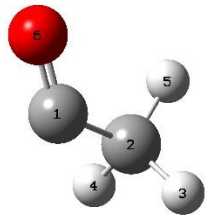
Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	2.241219	0.000000	0.000000
2	6	0	1.540632	1.218452	0.000000
3	6	0	0.149200	1.224258	0.000000
4	6	0	-0.581321	0.000000	0.000000
5	6	0	0.149200	-1.224258	0.000000
6	6	0	1.540632	-1.218452	0.000000
7	1	0	3.333777	0.000000	0.000000
8	1	0	2.089860	2.162994	0.000000
9	1	0	-0.410468	2.161663	0.000000
10	1	0	-0.410468	-2.161663	0.000000
11	1	0	2.089860	-2.162994	0.000000
12	16	0	-2.308121	0.000000	0.000000

Sum of electronic and zero-point Energies= -629.314708
Sum of electronic and thermal Energies= -629.308953
Sum of electronic and thermal Enthalpies= -629.308009

Sum of electronic and thermal Free Energies= -629.345334

Acyl Radical
(U)CAM-B3LYP/6-311G++(d,p)

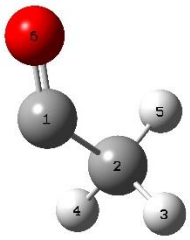


Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-0.245246	0.426998	0.000000
2	6	0	1.164048	-0.097086	0.000000
3	1	0	1.679499	0.292336	-0.878904
4	1	0	1.679498	0.292333	0.878906
5	1	0	1.177736	-1.190095	-0.000002
6	8	0	-1.256193	-0.171755	0.000000

Sum of electronic and zero-point Energies= -153.114980
Sum of electronic and thermal Energies= -153.111027
Sum of electronic and thermal Enthalpies= -153.110083
Sum of electronic and thermal Free Energies= -153.140620

Acyl Radical
(U)B3LYP/6-311G++(d,p)



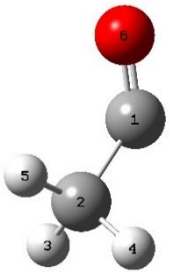
Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-0.245924	0.428320	0.000163
2	6	0	1.168636	-0.097663	-0.000017
3	1	0	1.683773	0.291500	-0.881156
4	1	0	1.686292	0.296972	0.877244

5	1	0	1.187732	-1.192312	0.003496
6	8	0	-1.261758	-0.172512	-0.000058

Sum of electronic and zero-point Energies= -153.188986
Sum of electronic and thermal Energies= -153.185029
Sum of electronic and thermal Enthalpies= -153.184084
Sum of electronic and thermal Free Energies= -153.214604

Acyl Radical
(U)MN12SX/6-311G++(d,p)

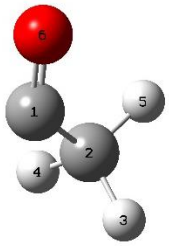


Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-0.246776	0.431492	-0.000001
2	6	0	1.161571	-0.098273	0.000000
3	1	0	1.679985	0.294250	-0.880597
4	1	0	1.679969	0.294220	0.880620
5	1	0	1.178839	-1.195778	-0.000018
6	8	0	-1.253446	-0.174001	0.000000

Sum of electronic and zero-point Energies= -153.051430
Sum of electronic and thermal Energies= -153.047470
Sum of electronic and thermal Enthalpies= -153.046525
Sum of electronic and thermal Free Energies= -153.077058

Acyl Radical
(U)PBE0/6-311G++(d,p)

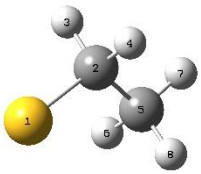


Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-0.240336	0.429399	-0.000001
2	6	0	1.169263	-0.099395	0.000001
3	1	0	1.691465	0.298198	-0.883409
4	1	0	1.691476	0.298233	0.883386
5	1	0	1.193219	-1.202764	0.000018
6	8	0	-1.268715	-0.171712	0.000000

Sum of electronic and zero-point Energies= -153.004555
Sum of electronic and thermal Energies= -153.000578
Sum of electronic and thermal Enthalpies= -152.999634
Sum of electronic and thermal Free Energies= -153.030161

Ethanethiyl Radical
(U)CAM-B3LYP/6-311G++(d,p)

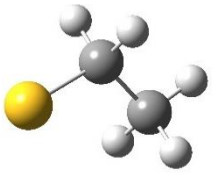


Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	16	0	-1.188770	-0.159031	0.000008
2	6	0	0.437230	0.620632	-0.000008
3	1	0	0.458253	1.285140	-0.869894
4	1	0	0.458261	1.285155	0.869866
5	6	0	1.619193	-0.335642	-0.000005
6	1	0	1.602216	-0.977955	-0.881714
7	1	0	2.560830	0.220146	-0.000015
8	1	0	1.602225	-0.977938	0.881716

Sum of electronic and zero-point Energies= -477.300380
Sum of electronic and thermal Energies= -477.296171
Sum of electronic and thermal Enthalpies= -477.295226
Sum of electronic and thermal Free Energies= -477.327276

Ethanethiyl Radical
(U)B3LYP/6-311G++(d,p)

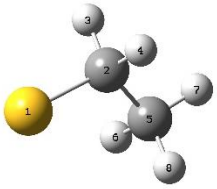


Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	16	0	-1.197704	-0.159033	0.000004
2	6	0	0.442262	0.620701	-0.000005
3	1	0	0.461099	1.286986	-0.871165
4	1	0	0.461104	1.286996	0.871148
5	6	0	1.630634	-0.336645	-0.000003
6	1	0	1.616331	-0.979265	-0.883104
7	1	0	2.571014	0.224715	-0.000019
8	1	0	1.616346	-0.979241	0.883116

Sum of electronic and zero-point Energies= -477.362590
Sum of electronic and thermal Energies= -477.358335
Sum of electronic and thermal Enthalpies= -477.357390
Sum of electronic and thermal Free Energies= -477.389529

Ethanethiyl Radical
(U)MN12SX/6-311G++(d,p)

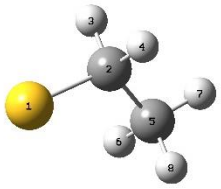


Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	16	0	-1.182867	-0.159488	0.000008
2	6	0	0.430502	0.617643	-0.000008
3	1	0	0.454429	1.291868	-0.871733
4	1	0	0.454437	1.291883	0.871705
5	6	0	1.613437	-0.333511	-0.000005
6	1	0	1.596987	-0.979644	-0.884172
7	1	0	2.559388	0.222539	-0.000015
8	1	0	1.596996	-0.979628	0.884173

Sum of electronic and zero-point Energies= -477.214453
Sum of electronic and thermal Energies= -477.210218
Sum of electronic and thermal Enthalpies= -477.209274
Sum of electronic and thermal Free Energies= -477.241361

Ethanethiyl Radical
(U)PBE0/6-311G++(d,p)

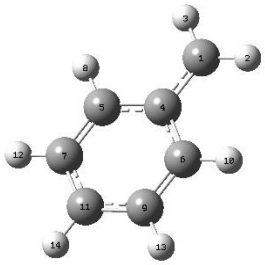


Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	16	0	-1.196825	-0.159662	0.000008
2	6	0	0.438239	0.616673	-0.000008
3	1	0	0.453659	1.295050	-0.874040
4	1	0	0.453667	1.295065	0.874012
5	6	0	1.632196	-0.334084	-0.000005
6	1	0	1.620574	-0.982031	-0.888654
7	1	0	2.578111	0.232991	-0.000015
8	1	0	1.620582	-0.982014	0.888656

Sum of electronic and zero-point Energies= -477.053347
Sum of electronic and thermal Energies= -477.049017
Sum of electronic and thermal Enthalpies= -477.048073
Sum of electronic and thermal Free Energies= -477.080344

Benzyl Radical
(U)CAM-B3LYP/6-311G++(d,p)



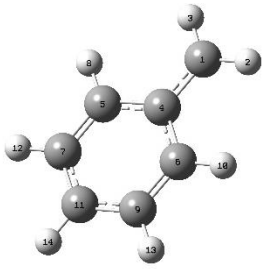
Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z

1	6	0	2.390611	0.000000	0.000000
2	1	0	2.948401	0.927338	0.000004
3	1	0	2.948384	-0.927348	0.000004
4	6	0	0.988739	0.000003	-0.000001
5	6	0	0.250852	-1.211936	-0.000002
6	6	0	0.250847	1.211940	0.000001
7	6	0	-1.127903	-1.205764	0.000001
8	1	0	0.790817	-2.152045	-0.000002
9	6	0	-1.127906	1.205762	-0.000002
10	1	0	0.790810	2.152050	0.000001
11	6	0	-1.829615	-0.000003	0.000001
12	1	0	-1.669763	-2.144311	0.000002
13	1	0	-1.669772	2.144305	-0.000001
14	1	0	-2.912631	-0.000004	0.000002

Sum of electronic and zero-point Energies= -270.704221
Sum of electronic and thermal Energies= -270.698601
Sum of electronic and thermal Enthalpies= -270.697657
Sum of electronic and thermal Free Energies= -270.733855

Benzyl Radical
(U)B3LYP/6-311G++(d,p)



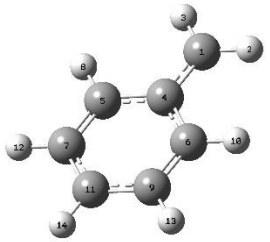
Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	2.399030	0.000009	0.000135
2	1	0	2.958706	0.927072	0.000023
3	1	0	2.958778	-0.927027	-0.000318
4	6	0	0.994268	-0.000041	-0.000041
5	6	0	0.251495	-1.216946	-0.000028
6	6	0	0.251516	1.216921	-0.000045
7	6	0	-1.132082	-1.210346	0.000016
8	1	0	0.790839	-2.158232	-0.000065
9	6	0	-1.132052	1.210375	-0.000011
10	1	0	0.790910	2.158181	-0.000066
11	6	0	-1.837124	0.000017	0.000036
12	1	0	-1.674369	-2.149603	-0.000011

13	1	0	-1.674315	2.149645	-0.000010
14	1	0	-2.920849	0.000020	0.000077

Sum of electronic and zero-point Energies= -270.873205
Sum of electronic and thermal Energies= -270.867512
Sum of electronic and thermal Enthalpies= -270.866568
Sum of electronic and thermal Free Energies= -270.902892

Benzyl Radical
(U)MN12SX/6-311G++(d,p)

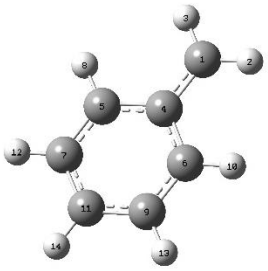


Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	2.391244	0.000004	0.000009
2	1	0	2.952191	0.930041	0.000013
3	1	0	2.952134	-0.930071	0.000021
4	6	0	0.990161	0.000008	-0.000023
5	6	0	0.251045	-1.213230	-0.000003
6	6	0	0.251027	1.213242	0.000001
7	6	0	-1.128543	-1.206718	0.000003
8	1	0	0.794856	-2.156881	0.000002
9	6	0	-1.128555	1.206712	0.000000
10	1	0	0.794835	2.156894	0.000006
11	6	0	-1.831345	-0.000010	0.000003
12	1	0	-1.672654	-2.149490	0.000007
13	1	0	-1.672682	2.149475	0.000003
14	1	0	-2.918889	-0.000016	0.000010

Sum of electronic and zero-point Energies= -270.626481
Sum of electronic and thermal Energies= -270.620743
Sum of electronic and thermal Enthalpies= -270.619798
Sum of electronic and thermal Free Energies= -270.656196

Benzyl Radical
(U)PBE0/6-311G++(d,p)



Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	2.406849	0.000001	-0.000001
2	1	0	2.970102	0.934635	-0.000013
3	1	0	2.970079	-0.934648	0.000014
4	6	0	0.998906	0.000006	-0.000010
5	6	0	0.252929	-1.221887	0.000004
6	6	0	0.252919	1.221895	0.000005
7	6	0	-1.136379	-1.215440	0.000000
8	1	0	0.797920	-2.169882	0.000013
9	6	0	-1.136386	1.215435	0.000001
10	1	0	0.797908	2.169892	0.000013
11	6	0	-1.844482	-0.000006	-0.000004
12	1	0	-1.682756	-2.162083	0.000004
13	1	0	-1.682774	2.162072	0.000005
14	1	0	-2.936608	-0.000007	-0.000009

Sum of electronic and zero-point Energies= -270.507371
Sum of electronic and thermal Energies= -270.501495
Sum of electronic and thermal Enthalpies= -270.500551
Sum of electronic and thermal Free Energies= -270.537181

Hydrogen Atom
(U)CAM-B3LYP/6-311G++(d,p)

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	1	0	0.000000	0.000000	0.000000

Sum of electronic and zero-point Energies= -0.498913

Sum of electronic and thermal Energies= -0.497497
Sum of electronic and thermal Enthalpies= -0.496553
Sum of electronic and thermal Free Energies= -0.509568

Hydrogen Atom
(U)B3LYP/6-311G++(d,p)

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	1	0	0.000000	0.000000	0.000000

Sum of electronic and zero-point Energies= -0.502257
Sum of electronic and thermal Energies= -0.500841
Sum of electronic and thermal Enthalpies= -0.499897
Sum of electronic and thermal Free Energies= -0.512911

Hydrogen Atom
(U)MN12SX/6-311G++(d,p)

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	1	0	0.000000	0.000000	0.000000

Sum of electronic and zero-point Energies= -0.495725
Sum of electronic and thermal Energies= -0.494309
Sum of electronic and thermal Enthalpies= -0.493364
Sum of electronic and thermal Free Energies= -0.506379

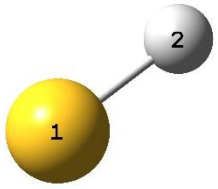
Hydrogen Atom
(U)PBE0/6-311G++(d,p)

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	1	0	0.000000	0.000000	0.000000

Sum of electronic and zero-point Energies= -0.499812
Sum of electronic and thermal Energies= -0.498396
Sum of electronic and thermal Enthalpies= -0.497452
Sum of electronic and thermal Free Energies= -0.510466

Hydrogen Sulfide Radical
(U)CAM-B3LYP/6-311G++(d,p)

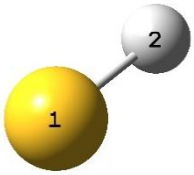


Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	16	0	0.000000	0.000000	0.079308
2	1	0	0.000000	0.000000	-1.268931

Sum of electronic and zero-point Energies= -398.757479
Sum of electronic and thermal Energies= -398.755119
Sum of electronic and thermal Enthalpies= -398.754175
Sum of electronic and thermal Free Energies= -398.775985

Hydrogen Sulfide Radical
(U)B3LYP/6-311G++(d,p)



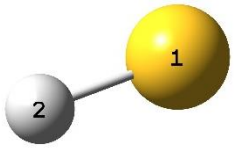
Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	16	0	0.000000	0.000000	0.079585

2	1	0	0.000000	0.000000	-1.273361

Sum of electronic and zero-point Energies= -398.766949
Sum of electronic and thermal Energies= -398.764588
Sum of electronic and thermal Enthalpies= -398.763644
Sum of electronic and thermal Free Energies= -398.785461

Hydrogen Sulfide Radical
(U)MN12SX/6-311G++(d,p)

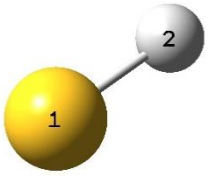


Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	16	0	0.000000	0.000000	0.079146
2	1	0	0.000000	0.000000	-1.266329

Sum of electronic and zero-point Energies= -398.701467
Sum of electronic and thermal Energies= -398.699107
Sum of electronic and thermal Enthalpies= -398.698163
Sum of electronic and thermal Free Energies= -398.719969

Hydrogen Sulfide Radical
(U)PBE0/6-311G++(d,p)

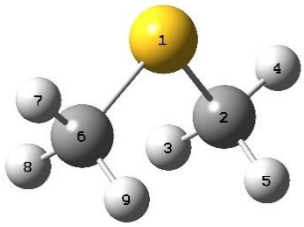


Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	16	0	0.000000	0.000000	0.080153
2	1	0	0.000000	0.000000	-1.282448

Sum of electronic and zero-point Energies= -398.570167
Sum of electronic and thermal Energies= -398.567807
Sum of electronic and thermal Enthalpies= -398.566863
Sum of electronic and thermal Free Energies= -398.588693

Dimethylsulfane
(U)MN12SX/6-311G++(2df,2p)//(U)MN12SX/6-31G(d)

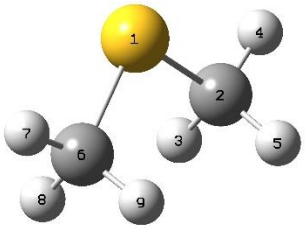


Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	16	0	0.000000	0.000000	0.663897
2	6	0	0.000000	1.365026	-0.512435
3	1	0	-0.895590	1.347094	-1.148119
4	1	0	0.000000	2.299986	0.059670
5	1	0	0.895590	1.347094	-1.148119
6	6	0	0.000000	-1.365026	-0.512435
7	1	0	0.000000	-2.299986	0.059670
8	1	0	-0.895590	-1.347094	-1.148119
9	1	0	0.895590	-1.347094	-1.148119

Sum of electronic and zero-point Energies= -477.852481
Sum of electronic and thermal Energies= -477.847811
Sum of electronic and thermal Enthalpies= -477.846867
Sum of electronic and thermal Free Energies= -477.878502

Dimethylsulfane
(U)MN12SX/6-311G++(d,p)//(U)MN12SX/6-31G(d)



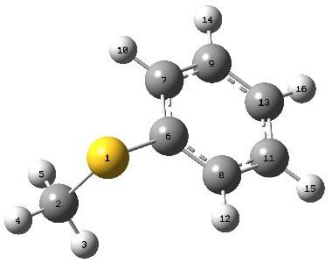
Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	16	0	0.000000	0.000000	0.663897
2	6	0	0.000000	1.365026	-0.512435
3	1	0	-0.895590	1.347094	-1.148119

4	1	0	0.000000	2.299986	0.059670
5	1	0	0.895590	1.347094	-1.148119
6	6	0	0.000000	-1.365026	-0.512435
7	1	0	0.000000	-2.299986	0.059670
8	1	0	-0.895590	-1.347094	-1.148119
9	1	0	0.895590	-1.347094	-1.148119

Sum of electronic and zero-point Energies= -477.841191
Sum of electronic and thermal Energies= -477.836403
Sum of electronic and thermal Enthalpies= -477.835459
Sum of electronic and thermal Free Energies= -477.867403

Methyl Phenyl Sulfane
(U)MN12SX/6-311G++(2df,2p)//(U)MN12SX/6-31G(d)



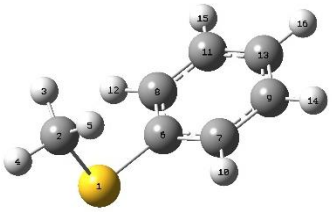
Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	16	0	1.887343	-0.000003	-0.628255
2	6	0	2.500989	0.000004	1.075230
3	1	0	2.169198	-0.895463	1.615711
4	1	0	3.596947	0.000004	1.029311
5	1	0	2.169199	0.895477	1.615703
6	6	0	0.136866	-0.000001	-0.286782
7	6	0	-0.554804	1.207198	-0.158830
8	6	0	-0.554806	-1.207199	-0.158826
9	6	0	-1.921413	1.205276	0.103639
10	1	0	-0.012575	2.146816	-0.271336
11	6	0	-1.921414	-1.205274	0.103643
12	1	0	-0.012578	-2.146818	-0.271330
13	6	0	-2.605494	0.000001	0.236951
14	1	0	-2.455256	2.151107	0.201713
15	1	0	-2.455259	-2.151104	0.201720
16	1	0	-3.676710	0.000002	0.440442

Sum of electronic and zero-point Energies= -669.444733
Sum of electronic and thermal Energies= -669.437227

Sum of electronic and thermal Enthalpies= -669.436283
Sum of electronic and thermal Free Energies= -669.477399

Methyl Phenyl Sulfane
(U)MN12SX/6-311G++(d,p)//(U)MN12SX/6-31G(d)

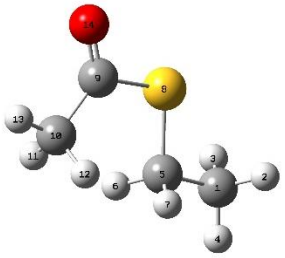


Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	16	0	1.887343	-0.000003	-0.628255
2	6	0	2.500989	0.000004	1.075230
3	1	0	2.169198	-0.895463	1.615711
4	1	0	3.596947	0.000004	1.029311
5	1	0	2.169199	0.895477	1.615703
6	6	0	0.136866	-0.000001	-0.286782
7	6	0	-0.554804	1.207198	-0.158830
8	6	0	-0.554806	-1.207199	-0.158826
9	6	0	-1.921413	1.205276	0.103639
10	1	0	-0.012575	2.146816	-0.271336
11	6	0	-1.921414	-1.205274	0.103643
12	1	0	-0.012578	-2.146818	-0.271330
13	6	0	-2.605494	0.000001	0.236951
14	1	0	-2.455256	2.151107	0.201713
15	1	0	-2.455259	-2.151104	0.201720
16	1	0	-3.676710	0.000002	0.440442

Sum of electronic and zero-point Energies= -669.420703
Sum of electronic and thermal Energies= -669.412963
Sum of electronic and thermal Enthalpies= -669.412019
Sum of electronic and thermal Free Energies= -669.455262

S-ethyl thioacetate
(U)MN12SX/6-311G++(2df,2p)//(U)MN12SX/6-31G(d)

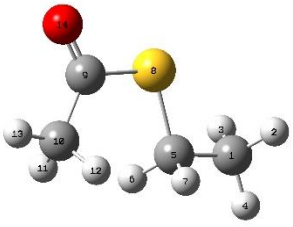


Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-2.809391	0.045052	-0.000013
2	1	0	-2.997458	-0.571644	0.887835
3	1	0	-2.997412	-0.571379	-0.888055
4	1	0	-3.531270	0.871190	0.000094
5	6	0	-1.389198	0.592438	0.000105
6	1	0	-1.223318	1.215710	-0.889393
7	1	0	-1.223373	1.215460	0.889789
8	16	0	-0.233796	-0.813847	-0.000057
9	6	0	1.395587	-0.076146	-0.000022
10	6	0	1.514072	1.429378	0.000116
11	1	0	1.033301	1.864388	-0.885540
12	1	0	1.033121	1.864271	0.885729
13	1	0	2.578407	1.684604	0.000231
14	8	0	2.350289	-0.811922	-0.000111

Sum of electronic and zero-point Energies= -630.396773
Sum of electronic and thermal Energies= -630.389277
Sum of electronic and thermal Enthalpies= -630.388333
Sum of electronic and thermal Free Energies= -630.428430

S-ethyl thioacetate
(U)MN12SX/6-311G++(d,p)//(U)MN12SX/6-31G(d)



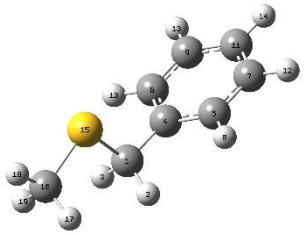
Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z

1	6	0	-2.809391	0.045052	-0.000013
2	1	0	-2.997458	-0.571644	0.887835
3	1	0	-2.997412	-0.571379	-0.888055
4	1	0	-3.531270	0.871190	0.000094
5	6	0	-1.389198	0.592438	0.000105
6	1	0	-1.223318	1.215710	-0.889393
7	1	0	-1.223373	1.215460	0.889789
8	16	0	-0.233796	-0.813847	-0.000057
9	6	0	1.395587	-0.076146	-0.000022
10	6	0	1.514072	1.429378	0.000116
11	1	0	1.033301	1.864388	-0.885540
12	1	0	1.033121	1.864271	0.885729
13	1	0	2.578407	1.684604	0.000231
14	8	0	2.350289	-0.811922	-0.000111

Sum of electronic and zero-point Energies= -630.376713
Sum of electronic and thermal Energies= -630.369019
Sum of electronic and thermal Enthalpies= -630.368075
Sum of electronic and thermal Free Energies= -630.408861

Benzyl(methyl)sulfane
(U)MN12SX/6-311G++(2df,2p)//(U)MN12SX/6-31G(d)



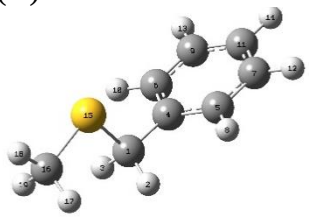
Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-1.020994	0.000501	0.819424
2	1	0	-1.267345	0.890208	1.418409
3	1	0	-1.267418	-0.888633	1.419236
4	6	0	0.434068	0.000256	0.441882
5	6	0	1.115772	1.202816	0.243932
6	6	0	1.115399	-1.202583	0.244305
7	6	0	2.455610	1.203946	-0.128166
8	1	0	0.585425	2.146991	0.382793
9	6	0	2.455231	-1.204256	-0.127790
10	1	0	0.584747	-2.146544	0.383456
11	6	0	3.129155	-0.000287	-0.313687
12	1	0	2.977223	2.150210	-0.274120

13	1	0	2.976548	-2.150729	-0.273448
14	1	0	4.180375	-0.000493	-0.603114
15	16	0	-2.049854	-0.000183	-0.684029
16	6	0	-3.669737	-0.000054	0.107191
17	1	0	-3.815541	0.895540	0.726080
18	1	0	-4.428058	-0.000472	-0.684179
19	1	0	-3.815317	-0.895185	0.726803

Sum of electronic and zero-point Energies= -708.703665
Sum of electronic and thermal Energies= -708.694917
Sum of electronic and thermal Enthalpies= -708.693973
Sum of electronic and thermal Free Energies= -708.738012

Benzyl(methyl)sulfane
(U)MN12SX/6-311G++(d,p)//(U)MN12SX/6-31G(d)

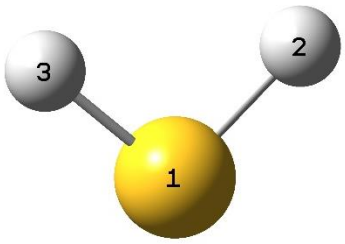


Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-1.020994	0.000501	0.819424
2	1	0	-1.267345	0.890208	1.418409
3	1	0	-1.267418	-0.888633	1.419236
4	6	0	0.434068	0.000256	0.441882
5	6	0	1.115772	1.202816	0.243932
6	6	0	1.115399	-1.202583	0.244305
7	6	0	2.455610	1.203946	-0.128166
8	1	0	0.585425	2.146991	0.382793
9	6	0	2.455231	-1.204256	-0.127790
10	1	0	0.584747	-2.146544	0.383456
11	6	0	3.129155	-0.000287	-0.313687
12	1	0	2.977223	2.150210	-0.274120
13	1	0	2.976548	-2.150729	-0.273448
14	1	0	4.180375	-0.000493	-0.603114
15	16	0	-2.049854	-0.000183	-0.684029
16	6	0	-3.669737	-0.000054	0.107191
17	1	0	-3.815541	0.895540	0.726080
18	1	0	-4.428058	-0.000472	-0.684179
19	1	0	-3.815317	-0.895185	0.726803

Sum of electronic and zero-point Energies= -708.677898
Sum of electronic and thermal Energies= -708.668956
Sum of electronic and thermal Enthalpies= -708.668012
Sum of electronic and thermal Free Energies= -708.712873

Hydrogen Sulfide
(U)MN12SX/6-311G++(2df,2p)//(U)MN12SX/6-31G(d)

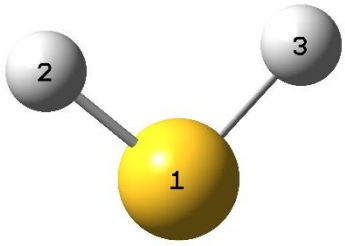


Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	16	0	0.000000	0.000000	0.102721
2	1	0	0.000000	0.971618	-0.821771
3	1	0	0.000000	-0.971618	-0.821771

Sum of electronic and zero-point Energies= -399.346573
Sum of electronic and thermal Energies= -399.343724
Sum of electronic and thermal Enthalpies= -399.342780
Sum of electronic and thermal Free Energies= -399.366123

Hydrogen Sulfide
(U)MN12SX/6-311G++(d,p)//(U)MN12SX/6-31G(d)

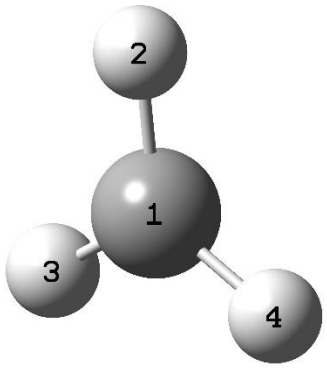


Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	16	0	0.000000	0.000000	0.102721
2	1	0	0.000000	0.971618	-0.821771
3	1	0	0.000000	-0.971618	-0.821771

Sum of electronic and zero-point Energies= -399.340736
Sum of electronic and thermal Energies= -399.337887
Sum of electronic and thermal Enthalpies= -399.336943
Sum of electronic and thermal Free Energies= -399.360287

Methyl Radical
(U)MN12SX/6-311G++(2df,2p)//(U)MN12SX/6-31G(d)

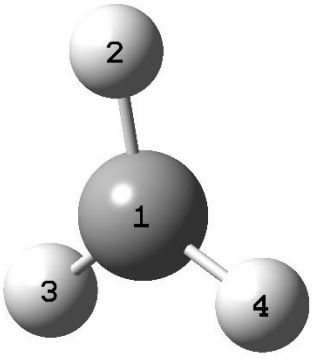


Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.000000	0.000000	0.000184
2	1	0	0.000000	1.084510	-0.000367
3	1	0	-0.939213	-0.542255	-0.000367
4	1	0	0.939213	-0.542255	-0.000367

Sum of electronic and zero-point Energies= -39.772765
Sum of electronic and thermal Energies= -39.769650
Sum of electronic and thermal Enthalpies= -39.768706
Sum of electronic and thermal Free Energies= -39.791564

Methyl Radical
(U)MN12SX/6-311G++(d,p)//(U)MN12SX/6-31G(d)

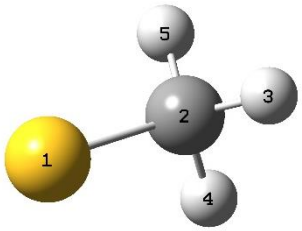


Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.000000	0.000000	0.000184
2	1	0	0.000000	1.084510	-0.000367
3	1	0	-0.939213	-0.542255	-0.000367
4	1	0	0.939213	-0.542255	-0.000367

Sum of electronic and zero-point Energies= -39.769245
Sum of electronic and thermal Energies= -39.766066
Sum of electronic and thermal Enthalpies= -39.765122
Sum of electronic and thermal Free Energies= -39.788093

Methanethiyl Radical
(U)MN12SX/6-311G++(2df,2p)//(U)MN12SX/6-31G(d)

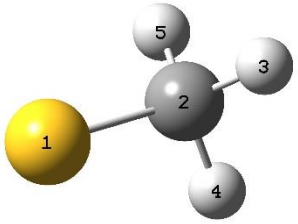


Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	16	0	0.689142	0.000035	-0.001870
2	6	0	-1.096893	0.000406	-0.008986
3	1	0	-1.509875	-0.887752	-0.503294
4	1	0	-1.425376	-0.028793	1.043307
5	1	0	-1.509665	0.913547	-0.456176

Sum of electronic and zero-point Energies= -437.964861
Sum of electronic and thermal Energies= -437.961738
Sum of electronic and thermal Enthalpies= -437.960794
Sum of electronic and thermal Free Energies= -437.989096

Methanethiyl Radical
(U)MN12SX/6-311G++(d,p)//(U)MN12SX/6-31G(d)

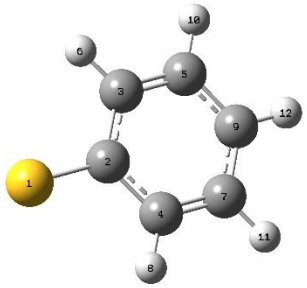


Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	16	0	0.689142	0.000035	-0.001870
2	6	0	-1.096893	0.000406	-0.008986
3	1	0	-1.509875	-0.887752	-0.503294
4	1	0	-1.425376	-0.028793	1.043307
5	1	0	-1.509665	0.913547	-0.456176

Sum of electronic and zero-point Energies= -437.957146
Sum of electronic and thermal Energies= -437.954047
Sum of electronic and thermal Enthalpies= -437.953103
Sum of electronic and thermal Free Energies= -437.981372

Phenylthiyl Radical
(U)MN12SX/6-311G++(2df,2p)//(U)MN12SX/6-31G(d)



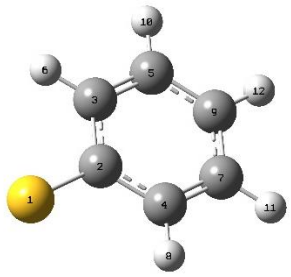
Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	16	0	0.000000	0.000000	2.292781
2	6	0	0.000000	0.000000	0.579138
3	6	0	0.000000	1.217336	-0.147477
4	6	0	0.000000	-1.217336	-0.147477
5	6	0	0.000000	1.212221	-1.531191
6	1	0	0.000000	2.154003	0.410414
7	6	0	0.000000	-1.212221	-1.531191
8	1	0	0.000000	-2.154003	0.410414
9	6	0	0.000000	0.000000	-2.226496
10	1	0	0.000000	2.154424	-2.079992
11	1	0	0.000000	-2.154424	-2.079992
12	1	0	0.000000	0.000000	-3.317179

Sum of electronic and zero-point Energies= -629.555775
Sum of electronic and thermal Energies= -629.550263
Sum of electronic and thermal Enthalpies= -629.549319

Sum of electronic and thermal Free Energies= -629.585545

Phenylthiyl Radical
(U)MN12SX/6-311G++(d,p)//(U)MN12SX/6-31G(d)

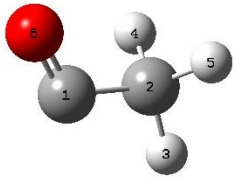


Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	16	0	0.000000	0.000000	2.292781
2	6	0	0.000000	0.000000	0.579138
3	6	0	0.000000	1.217336	-0.147477
4	6	0	0.000000	-1.217336	-0.147477
5	6	0	0.000000	1.212221	-1.531191
6	1	0	0.000000	2.154003	0.410414
7	6	0	0.000000	-1.212221	-1.531191
8	1	0	0.000000	-2.154003	0.410414
9	6	0	0.000000	0.000000	-2.226496
10	1	0	0.000000	2.154424	-2.079992
11	1	0	0.000000	-2.154424	-2.079992
12	1	0	0.000000	0.000000	-3.317179

Sum of electronic and zero-point Energies= -629.550004
Sum of electronic and thermal Energies= -629.544460
Sum of electronic and thermal Enthalpies= -629.543515
Sum of electronic and thermal Free Energies= -629.579790

Acyl Radical
(U)MN12SX/6-311G++(2df,2p)//(U)MN12SX/6-31G(d)



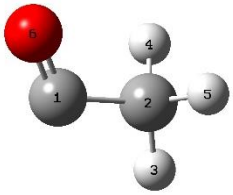
Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z

1	6	0	-0.250754	0.457233	-0.000186
2	6	0	1.163177	-0.090640	-0.000139
3	1	0	1.905001	0.711732	-0.012123
4	1	0	1.300921	-0.709563	0.896909
5	1	0	1.294092	-0.731008	-0.883052
6	8	0	-1.246819	-0.183840	0.000027

Sum of electronic and zero-point Energies= -153.059163
Sum of electronic and thermal Energies= -153.055247
Sum of electronic and thermal Enthalpies= -153.054302
Sum of electronic and thermal Free Energies= -153.084666

Acyl Radical
(U)MN12SX/6-311G++(d,p)//(U)MN12SX/6-31G(d)

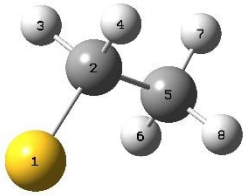


Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-0.250754	0.457233	-0.000186
2	6	0	1.163177	-0.090640	-0.000139
3	1	0	1.905001	0.711732	-0.012123
4	1	0	1.300921	-0.709563	0.896909
5	1	0	1.294092	-0.731008	-0.883052
6	8	0	-1.246819	-0.183840	0.000027

Sum of electronic and zero-point Energies= -153.050857
Sum of electronic and thermal Energies= -153.046777
Sum of electronic and thermal Enthalpies= -153.045833
Sum of electronic and thermal Free Energies= -153.077100

Ethanethiyl Radical
(U)MN12SX/6-311G++(2df,2p)//(U)MN12SX/6-31G(d)

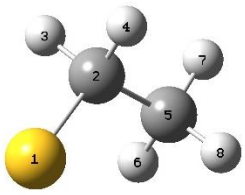


Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	16	0	1.184908	-0.159417	-0.000007
2	6	0	-0.432563	0.620130	0.000007
3	1	0	-0.460467	1.294302	0.873131
4	1	0	-0.460474	1.294316	-0.873106
5	6	0	-1.614560	-0.335702	0.000005
6	1	0	-1.596191	-0.982432	0.885933
7	1	0	-2.562460	0.220327	0.000016
8	1	0	-1.596202	-0.982413	-0.885938

Sum of electronic and zero-point Energies= -477.224385
Sum of electronic and thermal Energies= -477.219968
Sum of electronic and thermal Enthalpies= -477.219024
Sum of electronic and thermal Free Energies= -477.251468

Ethanethiyl Radical
(U)MN12SX/6-311G++(d,p)//(U)MN12SX/6-31G(d)



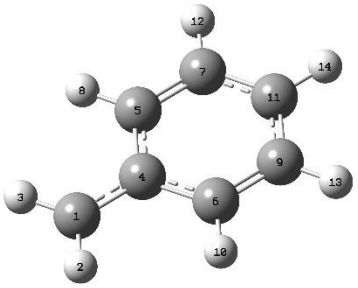
Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	16	0	1.184908	-0.159417	-0.000007
2	6	0	-0.432563	0.620130	0.000007
3	1	0	-0.460467	1.294302	0.873131
4	1	0	-0.460474	1.294316	-0.873106
5	6	0	-1.614560	-0.335702	0.000005
6	1	0	-1.596191	-0.982432	0.885933
7	1	0	-2.562460	0.220327	0.000016
8	1	0	-1.596202	-0.982413	-0.885938

Sum of electronic and zero-point Energies= -477.214461
Sum of electronic and thermal Energies= -477.210277
Sum of electronic and thermal Enthalpies= -477.209333
Sum of electronic and thermal Free Energies= -477.241311

Benzyl Radical

(U)MN12SX/6-311G++(2df,2p)//(U)MN12SX/6-31G(d)

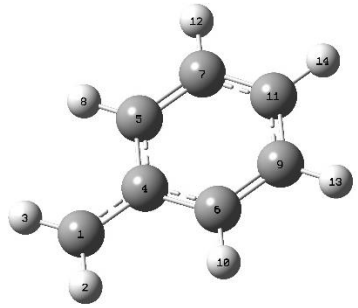


Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	2.394431	-0.000015	-0.000266
2	1	0	2.958591	-0.930741	0.000562
3	1	0	2.959013	0.930480	0.000384
4	6	0	0.991509	0.000108	0.000040
5	6	0	0.251290	1.214464	0.000017
6	6	0	0.251377	-1.214365	0.000065
7	6	0	-1.130296	1.208057	0.000013
8	1	0	0.795893	2.160045	0.000080
9	6	0	-1.130216	-1.208133	-0.000021
10	1	0	0.796076	-2.159895	0.000103
11	6	0	-1.834120	-0.000063	-0.000041
12	1	0	-1.674944	2.152847	0.000110
13	1	0	-1.674775	-2.152971	-0.000036
14	1	0	-2.923712	-0.000082	-0.000046

Sum of electronic and zero-point Energies= -270.645396
Sum of electronic and thermal Energies= -270.639826
Sum of electronic and thermal Enthalpies= -270.638882
Sum of electronic and thermal Free Energies= -270.674987

Benzyl Radical
(U)MN12SX/6-311G++(d,p)//(U)MN12SX/6-31G(d)



Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	2.394431	-0.000015	-0.000266
2	1	0	2.958591	-0.930741	0.000562
3	1	0	2.959013	0.930480	0.000384
4	6	0	0.991509	0.000108	0.000040
5	6	0	0.251290	1.214464	0.000017
6	6	0	0.251377	-1.214365	0.000065
7	6	0	-1.130296	1.208057	0.000013
8	1	0	0.795893	2.160045	0.000080
9	6	0	-1.130216	-1.208133	-0.000021
10	1	0	0.796076	-2.159895	0.000103
11	6	0	-1.834120	-0.000063	-0.000041
12	1	0	-1.674944	2.152847	0.000110
13	1	0	-1.674775	-2.152971	-0.000036
14	1	0	-2.923712	-0.000082	-0.000046

Sum of electronic and zero-point Energies= -270.626604
Sum of electronic and thermal Energies= -270.620917
Sum of electronic and thermal Enthalpies= -270.619973
Sum of electronic and thermal Free Energies= -270.656278

Hydrogen Atom
(U)MN12SX/6-311G++(2df,2p)//(U)MN12SX/6-31G(d)

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	1	0	0.000000	0.000000	0.000000

Sum of electronic and zero-point Energies= -0.495725
Sum of electronic and thermal Energies= -0.494309
Sum of electronic and thermal Enthalpies= -0.493364
Sum of electronic and thermal Free Energies= -0.506379

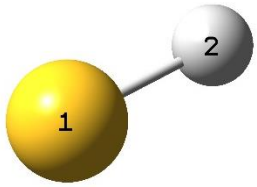
Hydrogen Atom
(U)MN12SX/6-311G++(d,p)//(U)MN12SX/6-31G(d)

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	1	0	0.000000	0.000000	0.000000

Sum of electronic and zero-point Energies= -0.495725
Sum of electronic and thermal Energies= -0.494309
Sum of electronic and thermal Enthalpies= -0.493364
Sum of electronic and thermal Free Energies= -0.506379

Hydrogen Sulfide Radical
(U)MN12SX/6-311G++(2df,2p)//(U)MN12SX/6-31G(d)

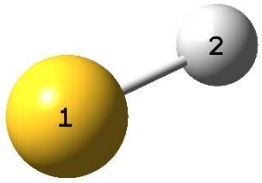


Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	16	0	0.000000	0.000000	0.079064
2	1	0	0.000000	0.000000	-1.265032

Sum of electronic and zero-point Energies= -398.705906
Sum of electronic and thermal Energies= -398.703545
Sum of electronic and thermal Enthalpies= -398.702601
Sum of electronic and thermal Free Energies= -398.724406

Hydrogen Sulfide Radical
(U)MN12SX/6-311G++(d,p)//(U)MN12SX/6-31G(d)

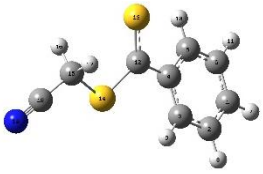


Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	16	0	0.000000	0.000000	0.079064
2	1	0	0.000000	0.000000	-1.265032

Sum of electronic and zero-point Energies= -398.701437
Sum of electronic and thermal Energies= -398.699077
Sum of electronic and thermal Enthalpies= -398.698133
Sum of electronic and thermal Free Energies= -398.719937

Cyanomethyl Benzodithioate
(U)MN12SX/6-311G++(d,p)//(U)MN12SX/6-31G(d)



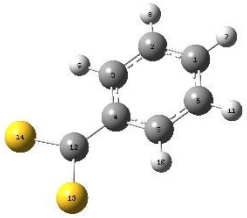
Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	3.915563	-0.895828	-0.073555
2	6	0	2.891070	-1.722750	0.377339
3	6	0	1.584586	-1.253342	0.426406
4	6	0	1.286845	0.060579	0.032317
5	6	0	2.329533	0.888583	-0.410289
6	6	0	3.629680	0.410061	-0.467561
7	1	0	4.939611	-1.267596	-0.114494
8	1	0	3.109644	-2.739811	0.702049
9	1	0	0.798900	-1.903043	0.812710
10	1	0	2.098651	1.907772	-0.718853
11	1	0	4.428036	1.060812	-0.823970
12	6	0	-0.094879	0.593540	0.075257
13	16	0	-0.457725	2.176534	0.310416
14	16	0	-1.295697	-0.660121	-0.193071
15	6	0	-2.834463	0.272545	0.043580
16	1	0	-2.895159	1.082004	-0.697612
17	1	0	-2.836139	0.736500	1.040345
18	6	0	-3.964526	-0.633437	-0.099311
19	7	0	-4.864179	-1.351280	-0.214687

Sum of electronic and zero-point Energies= -1197.862635
Sum of electronic and thermal Energies= -1197.851611
Sum of electronic and thermal Enthalpies= -1197.850667

Sum of electronic and thermal Free Energies= -1197.900894

Benzodithioyl Radical
(U)MN12SX/6-311G++(d,p)//(U)MN12SX/6-31G(d)

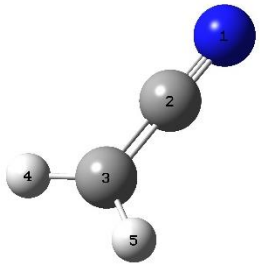


Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	3.134984	-0.000001	0.000011
2	6	0	2.439253	-1.207920	0.000004
3	6	0	1.052341	-1.209659	0.000000
4	6	0	0.343568	0.000000	0.000003
5	6	0	1.052342	1.209661	0.000010
6	6	0	2.439253	1.207920	0.000014
7	1	0	4.225358	0.000001	0.000015
8	1	0	2.982833	-2.152372	0.000002
9	1	0	0.503182	-2.152562	-0.000006
10	1	0	0.503182	2.152563	0.000013
11	1	0	2.982836	2.152370	0.000020
12	6	0	-1.121548	-0.000001	-0.000001
13	16	0	-2.101205	1.364034	-0.000012
14	16	0	-2.101204	-1.364034	-0.000006

Sum of electronic and zero-point Energies= -1065.798655
Sum of electronic and thermal Energies= -1065.791017
Sum of electronic and thermal Enthalpies= -1065.790073
Sum of electronic and thermal Free Energies= -1065.833046

Cyanomethyl Radical
(U)MN12SX/6-311G++(d,p)//(U)MN12SX/6-31G(d)

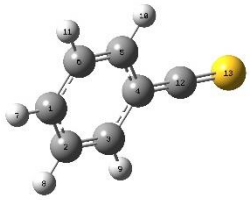


Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	7	0	0.000000	0.000000	1.359215
2	6	0	0.000000	0.000000	0.187034
3	6	0	0.000000	0.000000	-1.193106
4	1	0	0.000000	0.939455	-1.739038
5	1	0	0.000000	-0.939455	-1.739038

Sum of electronic and zero-point Energies= -131.983530
Sum of electronic and thermal Energies= -131.979934
Sum of electronic and thermal Enthalpies= -131.978989
Sum of electronic and thermal Free Energies= -132.007111

Thiobenzoyl Radical
(U)MN12SX/6-311G++(d,p)//(U)MN12SX/6-31G(d)



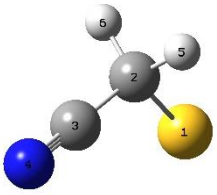
Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-2.729121	0.000089	0.000001
2	6	0	-2.021091	-1.206053	0.000000
3	6	0	-0.642032	-1.227499	0.000000
4	6	0	0.090415	-0.000092	0.000000
5	6	0	-0.641890	1.227423	0.000000
6	6	0	-2.020942	1.206153	0.000000
7	1	0	-3.817638	0.000154	0.000002
8	1	0	-2.561704	-2.153248	0.000001

9	1	0	-0.097718	-2.170406	0.000000
10	1	0	-0.097451	2.170257	0.000000
11	1	0	-2.561444	2.153411	0.000001
12	6	0	1.460007	-0.000112	-0.000001
13	16	0	3.010243	0.000024	0.000000

Sum of electronic and zero-point Energies= -667.597268
Sum of electronic and thermal Energies= -667.590446
Sum of electronic and thermal Enthalpies= -667.589501
Sum of electronic and thermal Free Energies= -667.629977

Cyanomethanethiyl Radical
(U)MN12SX/6-311G++(d,p)//(U)MN12SX/6-31G(d)

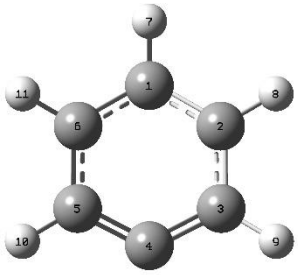


Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	16	0	1.460552	-0.300742	-0.000022
2	6	0	0.017876	0.772916	0.000030
3	6	0	-1.269436	0.086736	0.000051
4	7	0	-2.288886	-0.460102	-0.000030
5	1	0	0.081361	1.437324	0.877093
6	1	0	0.081363	1.437355	-0.877026

Sum of electronic and zero-point Energies= -530.151305
Sum of electronic and thermal Energies= -530.147040
Sum of electronic and thermal Enthalpies= -530.146096
Sum of electronic and thermal Free Energies= -530.179104

Phenyl Radical
(U)MN12SX/6-311G++(d,p)//(U)MN12SX/6-31G(d)

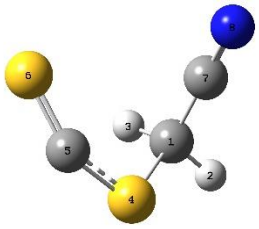


Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.000000	1.320432	0.000000
2	6	0	1.210877	0.630910	0.000000
3	6	0	1.220692	-0.768445	0.000000
4	6	0	0.000031	-1.399058	0.000000
5	6	0	-1.220695	-0.768443	0.000000
6	6	0	-1.210908	0.630849	0.000000
7	1	0	-0.000061	2.410481	0.000000
8	1	0	2.153620	1.180435	0.000000
9	1	0	2.158953	-1.324353	0.000000
10	1	0	-2.158883	-1.324475	0.000000
11	1	0	-2.153614	1.180435	0.000000

Sum of electronic and zero-point Energies= -231.331434
Sum of electronic and thermal Energies= -231.327049
Sum of electronic and thermal Enthalpies= -231.326105
Sum of electronic and thermal Free Energies= -231.359480

Cyanomethyl dithioyl Radical
(U)MN12SX/6-311G++(d,p)//(U)MN12SX/6-31G(d)



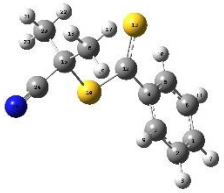
Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	1.353047	0.509617	0.708892
2	1	0	2.210719	1.186019	0.820772
3	1	0	0.936178	0.293441	1.701584
4	16	0	0.068512	1.452896	-0.267159
5	6	0	-1.260926	0.484077	-0.297256
6	16	0	-1.851847	-0.907017	0.153312
7	6	0	1.750526	-0.717063	0.047736
8	7	0	2.047224	-1.696187	-0.493862

Sum of electronic and zero-point Energies= -966.378805
Sum of electronic and thermal Energies= -966.372212
Sum of electronic and thermal Enthalpies= -966.371268

Sum of electronic and thermal Free Energies= -966.411392

2-cyanopropan-2-yl Benzodithioate Singlet
(U)MN12SX/6-311G++(d,p)//(U)MN12SX/6-31G(d)

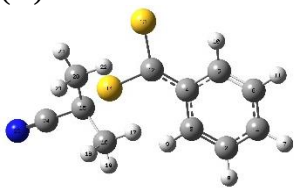


Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	4.337058	-0.904679	-0.059602
2	6	0	3.321236	-1.697307	0.465032
3	6	0	2.013730	-1.227782	0.499130
4	6	0	1.708550	0.055395	0.019302
5	6	0	2.743184	0.851136	-0.496004
6	6	0	4.042805	0.369729	-0.541384
7	1	0	5.360947	-1.277891	-0.090588
8	1	0	3.546594	-2.688488	0.858068
9	1	0	1.231772	-1.847914	0.936507
10	1	0	2.507083	1.847110	-0.869326
11	1	0	4.834154	0.993460	-0.956838
12	6	0	0.324379	0.598817	0.054846
13	16	0	0.019304	2.189270	0.328481
14	16	0	-0.825467	-0.676776	-0.294649
15	6	0	-2.552065	-0.042773	-0.001019
16	6	0	-2.772351	0.419582	1.444756
17	1	0	-2.193873	1.325716	1.647591
18	1	0	-3.837821	0.645300	1.584892
19	1	0	-2.486352	-0.363838	2.155480
20	6	0	-2.983148	1.002532	-1.037598
21	1	0	-4.049139	1.224911	-0.895385
22	1	0	-2.408196	1.923380	-0.904364
23	1	0	-2.838414	0.626716	-2.056647
24	6	0	-3.339926	-1.268279	-0.219573
25	7	0	-3.975553	-2.220942	-0.388289

Sum of electronic and zero-point Energies= -1276.373167
Sum of electronic and thermal Energies= -1276.359220
Sum of electronic and thermal Enthalpies= -1276.358276
Sum of electronic and thermal Free Energies= -1276.414489

2-cyanopropan-2-yl Benzodithioate Triplet
(U)MN12SX/6-311G++(d,p)//(U)MN12SX/6-31G(d)

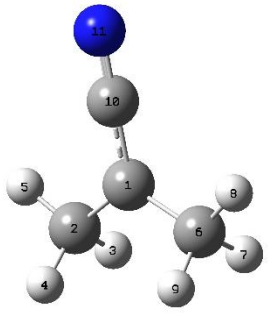


Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	3.960640	-1.193479	0.166564
2	6	0	2.872701	-1.850787	-0.408967
3	6	0	1.666439	-1.194710	-0.588323
4	6	0	1.513570	0.153207	-0.196164
5	6	0	2.626399	0.806420	0.378745
6	6	0	3.826519	0.139697	0.556170
7	1	0	4.907027	-1.714914	0.306079
8	1	0	2.969880	-2.889210	-0.726863
9	1	0	0.828027	-1.713128	-1.055921
10	1	0	2.530386	1.848829	0.688928
11	1	0	4.670942	0.664519	1.003882
12	6	0	0.278814	0.858654	-0.374268
13	16	0	-0.020993	2.526134	-0.165751
14	16	0	-1.193511	0.211105	-1.054061
15	6	0	-2.120553	-0.461769	0.447089
16	6	0	-1.359795	-1.648559	1.043460
17	1	0	-0.377301	-1.310911	1.397894
18	1	0	-1.919895	-2.052440	1.897642
19	1	0	-1.219263	-2.449977	0.308804
20	6	0	-2.353404	0.628995	1.492739
21	1	0	-2.955397	0.219218	2.314846
22	1	0	-1.389038	0.958928	1.898241
23	1	0	-2.875101	1.493913	1.067527
24	6	0	-3.397957	-0.907326	-0.116128
25	7	0	-4.402636	-1.261816	-0.569938

Sum of electronic and zero-point Energies= -1276.316349
Sum of electronic and thermal Energies= -1276.302341
Sum of electronic and thermal Enthalpies= -1276.301396
Sum of electronic and thermal Free Energies= -1276.358348

2-cyano-2-propanyl Radical
(U)MN12SX/6-311G++(d,p)//(U)MN12SX/6-31G(d)

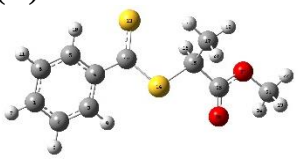


Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.309087	-0.000017	0.000319
2	6	0	1.061277	1.288651	-0.000063
3	1	0	1.717093	1.354954	0.883131
4	1	0	1.719360	1.353077	-0.881729
5	1	0	0.395934	2.158192	-0.001848
6	6	0	1.061716	-1.288413	-0.000032
7	1	0	1.719398	-1.353365	0.881846
8	1	0	0.396669	-2.158182	0.000568
9	1	0	1.717961	-1.353712	-0.883026
10	6	0	-1.080953	-0.000295	0.000032
11	7	0	-2.253312	-0.000074	-0.000068

Sum of electronic and zero-point Energies= -210.509424
Sum of electronic and thermal Energies= -210.503214
Sum of electronic and thermal Enthalpies= -210.502270
Sum of electronic and thermal Free Energies= -210.539296

2-((phenylcarbonothioyl)thio)propanoic acid Singlet
(U)MN12SX/6-311G++(d,p)//(U)MN12SX/6-31G(d)



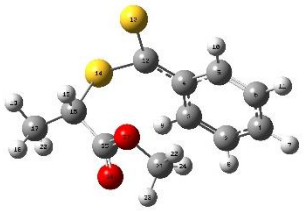
Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-4.797050	-1.094152	0.042028
2	6	0	-3.700779	-1.905012	-0.234122

3	6	0	-2.423744	-1.360261	-0.289416
4	6	0	-2.227470	0.013689	-0.082006
5	6	0	-3.341283	0.823303	0.184497
6	6	0	-4.611991	0.270918	0.252918
7	1	0	-5.797825	-1.524234	0.089129
8	1	0	-3.838845	-2.970744	-0.415926
9	1	0	-1.578016	-2.002823	-0.534434
10	1	0	-3.189468	1.890109	0.346616
11	1	0	-5.466466	0.911210	0.472607
12	6	0	-0.875499	0.625778	-0.151766
13	16	0	-0.626625	2.157472	-0.698380
14	16	0	0.358342	-0.475242	0.420318
15	6	0	1.894940	0.454480	0.149925
16	1	0	1.789299	1.014474	-0.791669
17	6	0	2.198515	1.428539	1.289121
18	1	0	3.122305	1.978250	1.069458
19	1	0	1.379392	2.149320	1.390489
20	1	0	2.320540	0.891542	2.238165
21	6	0	5.261220	-0.809534	-0.548868
22	1	0	6.078330	-0.169143	-0.890335
23	1	0	5.510383	-1.274618	0.412555
24	1	0	5.057611	-1.599526	-1.281747
25	6	0	3.013931	-0.559181	0.001546
26	8	0	2.939131	-1.737890	0.244654
27	8	0	4.130936	0.045276	-0.412036

Sum of electronic and zero-point Energies= -1372.650915
Sum of electronic and thermal Energies= -1372.635894
Sum of electronic and thermal Enthalpies= -1372.634950
Sum of electronic and thermal Free Energies= -1372.694222

2-((phenylcarbonothioyl)thio)propanoic acid Triplet
(U)MN12SX/6-311G++(d,p)//(U)MN12SX/6-31G(d)



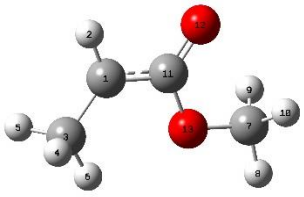
Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	3.602428	-0.771733	-0.570071
2	6	0	2.519527	-1.106822	-1.383927

3	6	0	1.324361	-0.411363	-1.293816
4	6	0	1.178695	0.653202	-0.375966
5	6	0	2.286734	0.985608	0.436257
6	6	0	3.473931	0.280309	0.338874
7	1	0	4.539031	-1.323538	-0.644569
8	1	0	2.606874	-1.925828	-2.098391
9	1	0	0.483401	-0.693612	-1.928256
10	1	0	2.195211	1.804984	1.152001
11	1	0	4.313503	0.552352	0.979602
12	6	0	-0.052710	1.366922	-0.242113
13	16	0	-0.435346	2.676707	0.775211
14	16	0	-1.553052	0.958117	-1.043422
15	6	0	-2.350572	-0.253526	0.118068
16	1	0	-2.584104	0.296146	1.039206
17	6	0	-3.590757	-0.793375	-0.571901
18	1	0	-4.136931	-1.458123	0.109147
19	1	0	-4.262609	0.021013	-0.868822
20	1	0	-3.311841	-1.374933	-1.458558
21	6	0	0.404802	-1.973947	1.824096
22	1	0	0.861701	-1.594995	2.741720
23	1	0	0.012310	-2.986988	1.974969
24	1	0	1.137235	-1.985999	1.006195
25	6	0	-1.349750	-1.350919	0.420950
26	8	0	-1.184478	-2.332937	-0.261596
27	8	0	-0.655465	-1.071289	1.522151

Sum of electronic and zero-point Energies= -1372.591741
Sum of electronic and thermal Energies= -1372.576427
Sum of electronic and thermal Enthalpies= -1372.575483
Sum of electronic and thermal Free Energies= -1372.635680

1-carboxyethanyl Radical
(U)MN12SX/6-311G++(d,p)//(U)MN12SX/6-31G(d)



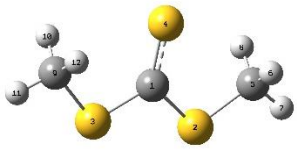
Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-1.365237	0.518863	-0.002912
2	1	0	-1.810567	1.512437	0.000942

3	6	0	-2.225922	-0.683502	0.000323
4	1	0	-2.847873	-0.719931	0.910132
5	1	0	-2.932347	-0.664388	-0.844681
6	1	0	-1.639319	-1.605737	-0.053340
7	6	0	2.025084	-0.765206	0.000336
8	1	0	2.298127	-1.824363	0.002915
9	1	0	2.428788	-0.267706	-0.890711
10	1	0	2.427349	-0.263619	0.889714
11	6	0	0.079240	0.513139	-0.000605
12	8	0	0.765797	1.520591	0.001320
13	8	0	0.608808	-0.728899	-0.001048

Sum of electronic and zero-point Energies= -306.770713
Sum of electronic and thermal Energies= -306.763655
Sum of electronic and thermal Enthalpies= -306.762711
Sum of electronic and thermal Free Energies= -306.802109

Dimethyl Trithiocarbonate Singlet
(U)MN12SX/6-311G++(d,p)//(U)MN12SX/6-31G(d)

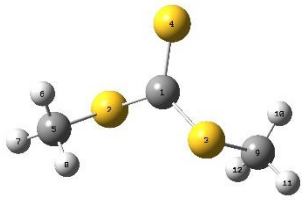


Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.000000	0.000000	0.025035
2	16	0	-0.000056	-1.426511	-0.998160
3	16	0	0.000056	1.426511	-0.998160
4	16	0	0.000000	0.000000	1.665563
5	6	0	0.000000	-2.757527	0.209773
6	1	0	-0.894269	-2.710422	0.841164
7	1	0	-0.000113	-3.688103	-0.369812
8	1	0	0.894410	-2.710519	0.840970
9	6	0	0.000000	2.757527	0.209773
10	1	0	0.894269	2.710422	0.841164
11	1	0	0.000113	3.688103	-0.369812
12	1	0	-0.894410	2.710519	0.840970

Sum of electronic and zero-point Energies= -1312.254613
Sum of electronic and thermal Energies= -1312.246483
Sum of electronic and thermal Enthalpies= -1312.245539
Sum of electronic and thermal Free Energies= -1312.287582

Dimethyl Trithiocarbonate Triplet
(U)MN12SX/6-311G++(d,p)//(U)MN12SX/6-31G(d)

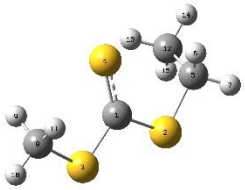


Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.000000	0.000000	0.290655
2	16	0	0.000000	1.542963	-0.515593
3	16	0	0.000000	-1.542963	-0.515593
4	16	0	0.000000	0.000000	1.983287
5	6	0	-1.760589	1.752382	-0.914153
6	1	0	-2.360205	1.774101	0.003267
7	1	0	-1.867814	2.707824	-1.441708
8	1	0	-2.100592	0.938472	-1.565421
9	6	0	1.760589	-1.752382	-0.914153
10	1	0	2.360205	-1.774101	0.003267
11	1	0	1.867814	-2.707824	-1.441708
12	1	0	2.100592	-0.938472	-1.565421

Sum of electronic and zero-point Energies= -1312.172556
Sum of electronic and thermal Energies= -1312.163284
Sum of electronic and thermal Enthalpies= -1312.162339
Sum of electronic and thermal Free Energies= -1312.208995

Ethyl Methyl Trithiocarbonate Singlet
(U)MN12SX/6-311G++(d,p)//(U)MN12SX/6-31G(d)



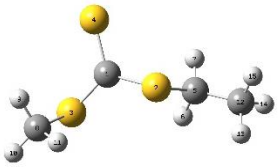
Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.331938	-0.020760	-0.126416
2	16	0	-0.988017	-1.169186	-0.283884
3	16	0	1.803121	-0.918865	0.208300

4	16	0	0.234498	1.610334	-0.283535
5	6	0	-2.452719	-0.107531	-0.427448
6	1	0	-2.215733	0.697680	-1.135217
7	1	0	-3.203357	-0.759219	-0.895949
8	6	0	3.047248	0.378397	0.214843
9	1	0	2.845357	1.107728	1.007045
10	1	0	4.003054	-0.123852	0.404196
11	1	0	3.080676	0.891670	-0.752507
12	6	0	-2.941442	0.433199	0.905175
13	1	0	-2.179678	1.066028	1.375424
14	1	0	-3.840655	1.044573	0.750538
15	1	0	-3.193452	-0.380948	1.595456

Sum of electronic and zero-point Energies= -1351.511440
Sum of electronic and thermal Energies= -1351.502087
Sum of electronic and thermal Enthalpies= -1351.501143
Sum of electronic and thermal Free Energies= -1351.546796

Ethyl Methyl Trithiocarbonate Triplet
(U)MN12SX/6-311G++(d,p)//(U)MN12SX/6-31G(d)

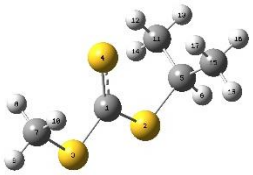


Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-0.484096	0.322867	0.009152
2	16	0	0.999243	-0.136044	0.793064
3	16	0	-1.582900	-0.785961	-0.759290
4	16	0	-0.848912	1.974567	-0.029615
5	6	0	2.176794	-0.195268	-0.611305
6	1	0	1.798922	-0.930482	-1.335424
7	1	0	2.177517	0.792630	-1.091842
8	6	0	-2.628669	-1.299184	0.636510
9	1	0	-3.156630	-0.434986	1.055980
10	1	0	-3.359997	-2.020740	0.252595
11	1	0	-2.018770	-1.777952	1.411613
12	6	0	3.557728	-0.572063	-0.104338
13	1	0	3.550829	-1.556868	0.380192
14	1	0	4.267325	-0.613134	-0.940435
15	1	0	3.931365	0.162431	0.620644

Sum of electronic and zero-point Energies= -1351.429195
Sum of electronic and thermal Energies= -1351.418734
Sum of electronic and thermal Enthalpies= -1351.417790
Sum of electronic and thermal Free Energies= -1351.467928

Methyl *iso*-Propyl Trithiocarbonate Singlet
(U)MN12SX/6-311G++(d,p)//(U)MN12SX/6-31G(d)

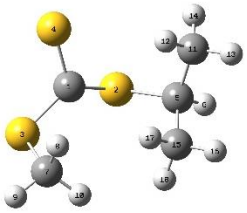


Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.585037	-0.031765	-0.000361
2	16	0	-0.674420	-1.248882	-0.001749
3	16	0	2.125003	-0.889954	0.000803
4	16	0	0.436317	1.603867	-0.000219
5	6	0	-2.313804	-0.415526	0.000315
6	1	0	-2.945779	-1.320285	0.000200
7	6	0	3.312133	0.458477	-0.000263
8	1	0	3.197023	1.081725	0.893415
9	1	0	4.300627	-0.015584	-0.000170
10	1	0	3.196661	1.080619	-0.894674
11	6	0	-2.604399	0.359349	1.279598
12	1	0	-1.994761	1.265544	1.351420
13	1	0	-3.661996	0.659680	1.278845
14	1	0	-2.425717	-0.257621	2.168376
15	6	0	-2.606605	0.361259	-1.277327
16	1	0	-3.664261	0.661371	-1.274473
17	1	0	-1.997177	1.267623	-1.348745
18	1	0	-2.429208	-0.254327	-2.167325

Sum of electronic and zero-point Energies= -1390.764414
Sum of electronic and thermal Energies= -1390.753660
Sum of electronic and thermal Enthalpies= -1390.752716
Sum of electronic and thermal Free Energies= -1390.801441

Methyl *iso*-Propyl Trithiocarbonate Triplet
(U)MN12SX/6-311G++(d,p)//(U)MN12SX/6-31G(d)

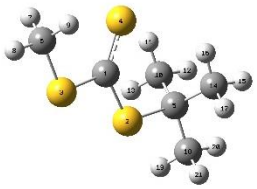


Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-0.572993	-0.500591	0.251631
2	16	0	0.815753	-0.267725	1.277799
3	16	0	-2.087752	0.351099	0.449473
4	16	0	-0.700992	-1.930180	-0.649892
5	6	0	2.080776	0.537939	0.194990
6	1	0	2.865670	0.778712	0.930564
7	6	0	-2.015642	1.665037	-0.800264
8	1	0	-1.744712	1.248638	-1.777737
9	1	0	-3.019939	2.101707	-0.862375
10	1	0	-1.302345	2.445728	-0.511912
11	6	0	2.634157	-0.427548	-0.843986
12	1	0	1.854850	-0.701414	-1.568874
13	1	0	3.457054	0.047246	-1.398194
14	1	0	3.011676	-1.348001	-0.382965
15	6	0	1.563238	1.817476	-0.439860
16	1	0	2.379429	2.336893	-0.961758
17	1	0	0.790577	1.583308	-1.185172
18	1	0	1.138377	2.502210	0.305277

Sum of electronic and zero-point Energies= -1390.688125
Sum of electronic and thermal Energies= -1390.676607
Sum of electronic and thermal Enthalpies= -1390.675663
Sum of electronic and thermal Free Energies= -1390.727963

tert-Butyl Methyl Trithiocarbonate Singlet
(U)MN12SX/6-311G++(d,p)//(U)MN12SX/6-31G(d)



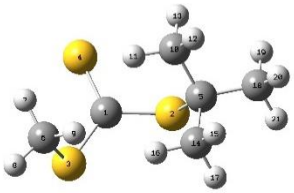
Standard orientation:

Center	Atomic	Atomic	Coordinates (Angstroms)

Number	Number	Type	X	Y	Z
1	6	0	-0.872841	0.008083	-0.000499
2	16	0	0.537988	-1.030835	-0.003232
3	16	0	-2.280318	-1.055819	0.001511
4	16	0	-0.957471	1.648165	-0.000255
5	6	0	2.092045	-0.012847	0.000484
6	6	0	-3.645431	0.112726	-0.000660
7	1	0	-3.619091	0.744746	-0.895369
8	1	0	-4.557046	-0.496664	-0.000634
9	1	0	-3.620319	0.746623	0.892746
10	6	0	2.217879	0.827446	-1.267125
11	1	0	1.459400	1.615180	-1.317136
12	1	0	3.208650	1.306183	-1.273193
13	1	0	2.137444	0.200138	-2.164192
14	6	0	2.214677	0.822986	1.271327
15	1	0	3.205534	1.301458	1.281674
16	1	0	1.456287	1.610762	1.322051
17	1	0	2.131713	0.192593	2.165995
18	6	0	3.166991	-1.106728	-0.000116
19	1	0	3.100196	-1.742884	-0.892980
20	1	0	4.155665	-0.626667	0.001548
21	1	0	3.098462	-1.745635	0.890637

Sum of electronic and zero-point Energies= -1430.024341
Sum of electronic and thermal Energies= -1430.012230
Sum of electronic and thermal Enthalpies= -1430.011286
Sum of electronic and thermal Free Energies= -1430.062800

tert-Butyl Methyl Trithiocarbonate Triplet
(U)MN12SX/6-311G++(d,p)//(U)MN12SX/6-31G(d)



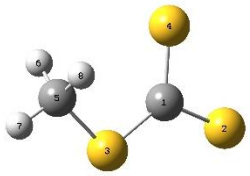
Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.915046	-0.488171	-0.383669
2	16	0	-0.697313	-0.692004	-0.995916
3	16	0	1.978475	0.843680	-0.739076
4	16	0	1.422911	-1.865038	0.472015
5	6	0	-1.811439	0.260752	0.165087

6	6	0	2.197190	1.606228	0.898765
7	1	0	2.522557	0.857990	1.630805
8	1	0	2.981270	2.366250	0.797059
9	1	0	1.274623	2.088243	1.247419
10	6	0	-1.478462	-0.079979	1.611128
11	1	0	-0.452258	0.216630	1.868601
12	1	0	-2.165350	0.458620	2.280801
13	1	0	-1.579547	-1.156279	1.804157
14	6	0	-1.646530	1.754538	-0.102887
15	1	0	-2.324708	2.325063	0.549873
16	1	0	-0.619885	2.086311	0.098154
17	1	0	-1.881690	2.003457	-1.145717
18	6	0	-3.220093	-0.202624	-0.199458
19	1	0	-3.352577	-1.275368	-0.007792
20	1	0	-3.953967	0.347149	0.407253
21	1	0	-3.447907	-0.008736	-1.256777

Sum of electronic and zero-point Energies= -1429.948958
Sum of electronic and thermal Energies= -1429.936322
Sum of electronic and thermal Enthalpies= -1429.935378
Sum of electronic and thermal Free Energies= -1429.988714

Methyl Carbonotrithioyl Radical
(U)MN12SX/6-311G++(d,p)//(U)MN12SX/6-31G(d)



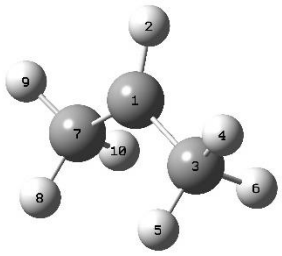
Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.353533	-0.060816	-0.000024
2	16	0	1.884748	-0.751993	-0.000051
3	16	0	-1.082052	-1.019053	0.000137
4	16	0	0.450659	1.613082	-0.000099
5	6	0	-2.371784	0.242299	0.000045
6	1	0	-2.309336	0.868124	-0.897789
7	1	0	-3.325334	-0.297687	-0.000044
8	1	0	-2.309487	0.868091	0.897914

Sum of electronic and zero-point Energies= -1272.381631
Sum of electronic and thermal Energies= -1272.375411
Sum of electronic and thermal Enthalpies= -1272.374467

Sum of electronic and thermal Free Energies= -1272.413401

iso-Propyl Radical
(U)MN12SX/6-311G++(d,p)//(U)MN12SX/6-31G(d)

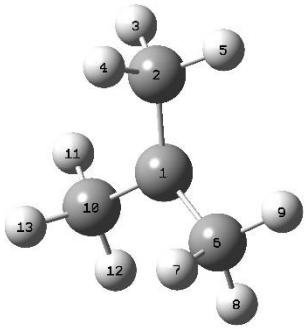


Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.000000	0.535873	-0.059756
2	1	0	0.000000	1.607836	0.136839
3	6	0	-1.288882	-0.197444	0.004833
4	1	0	-2.140967	0.437458	-0.270689
5	1	0	-1.286293	-1.071928	-0.665322
6	1	0	-1.500022	-0.592399	1.017859
7	6	0	1.288882	-0.197444	0.004833
8	1	0	1.286290	-1.071932	-0.665317
9	1	0	2.140966	0.437456	-0.270695
10	1	0	1.500025	-0.592393	1.017860

Sum of electronic and zero-point Energies= -118.290163
Sum of electronic and thermal Energies= -118.285186
Sum of electronic and thermal Enthalpies= -118.284242
Sum of electronic and thermal Free Energies= -118.316924

tert-Butyl Radical
(U)MN12SX/6-311G++(d,p)//(U)MN12SX/6-31G(d)



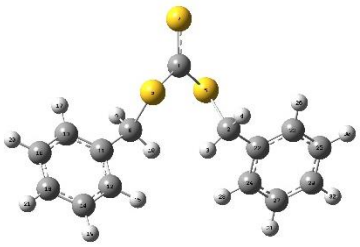
Standard orientation:

Center	Atomic	Atomic	Coordinates (Angstroms)

Number	Number	Type	X	Y	Z
1	6	0	0.000000	0.000000	0.153646
2	6	0	0.000000	1.479225	-0.016099
3	1	0	0.890439	1.940378	0.435800
4	1	0	0.000000	1.781990	-1.082301
5	1	0	-0.890439	1.940378	0.435800
6	6	0	-1.281047	-0.739613	-0.016099
7	1	0	-1.543249	-0.890995	-1.082301
8	1	0	-1.235197	-1.741332	0.435800
9	1	0	-2.125636	-0.199046	0.435800
10	6	0	1.281047	-0.739613	-0.016099
11	1	0	2.125636	-0.199046	0.435800
12	1	0	1.235197	-1.741332	0.435800
13	1	0	1.543249	-0.890995	-1.082301

Sum of electronic and zero-point Energies= -157.552792
Sum of electronic and thermal Energies= -157.546623
Sum of electronic and thermal Enthalpies= -157.545679
Sum of electronic and thermal Free Energies= -157.580708

Dibenzyl Trithiocarbonate Singlet
(U)MN12SX/6-311G++(d,p)//(U)MN12SX/6-31G(d)



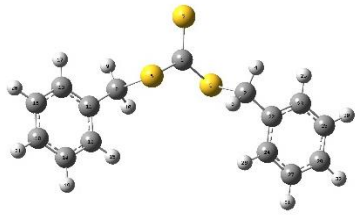
Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-0.000012	2.186600	0.000050
2	6	0	1.626428	-0.043607	0.612112
3	1	0	0.799445	-0.762659	0.597052
4	1	0	1.642687	0.435572	1.600265
5	16	0	1.384273	1.291911	-0.628871
6	16	0	-1.384339	1.291943	0.629006
7	16	0	0.000022	3.820882	-0.000025
8	6	0	-1.626538	-0.043367	-0.612178
9	1	0	-1.643002	0.435991	-1.600243
10	1	0	-0.799468	-0.762323	-0.597393
11	6	0	-2.928959	-0.729993	-0.311791

12	6	0	-2.943173	-1.967129	0.334518
13	6	0	-4.142983	-0.131141	-0.659610
14	6	0	-4.147360	-2.605490	0.612850
15	1	0	-1.998583	-2.437062	0.616061
16	6	0	-5.346879	-0.766699	-0.380184
17	1	0	-4.138265	0.842859	-1.152860
18	6	0	-5.351335	-2.006581	0.254894
19	1	0	-4.144938	-3.575208	1.110779
20	1	0	-6.287575	-0.292977	-0.661048
21	1	0	-6.295791	-2.506032	0.471415
22	6	0	2.928948	-0.730067	0.311754
23	6	0	4.142923	-0.131053	0.659459
24	6	0	2.943263	-1.967266	-0.334435
25	6	0	5.346872	-0.766515	0.380033
26	1	0	4.138131	0.843001	1.152601
27	6	0	4.147500	-2.605532	-0.612765
28	1	0	1.998704	-2.437324	-0.615878
29	6	0	5.351427	-2.006462	-0.254920
30	1	0	6.287534	-0.292667	0.660799
31	1	0	4.145159	-3.575297	-1.110602
32	1	0	6.295927	-2.505836	-0.471433

Sum of electronic and zero-point Energies= -1773.909936
Sum of electronic and thermal Energies= -1773.892928
Sum of electronic and thermal Enthalpies= -1773.891984
Sum of electronic and thermal Free Energies= -1773.957813

Dibenzyl Trithiocarbonate Triplet
(U)MN12SX/6-311G++(d,p)//(U)MN12SX/6-31G(d)



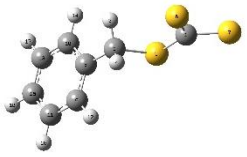
Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.000001	1.626269	0.000042
2	6	0	2.358216	0.410956	0.847817
3	1	0	1.691779	-0.149218	1.517858
4	1	0	2.631566	1.358103	1.331149
5	16	0	1.384495	0.815772	-0.670332
6	16	0	-1.384516	0.815783	0.670384

7	16	0	-0.000015	3.318935	-0.000004
8	6	0	-2.358167	0.410910	-0.847795
9	1	0	-2.631490	1.358038	-1.331180
10	1	0	-1.691701	-0.149294	-1.517782
11	6	0	-3.563371	-0.391316	-0.461213
12	6	0	-3.473697	-1.779575	-0.326961
13	6	0	-4.778762	0.238392	-0.182938
14	6	0	-4.581311	-2.525057	0.059953
15	1	0	-2.523239	-2.276424	-0.532101
16	6	0	-5.887909	-0.506019	0.203427
17	1	0	-4.852966	1.323850	-0.274427
18	6	0	-5.791611	-1.889618	0.325014
19	1	0	-4.500412	-3.608326	0.154096
20	1	0	-6.832887	-0.003417	0.410902
21	1	0	-6.661215	-2.473741	0.627189
22	6	0	3.563398	-0.391290	0.461210
23	6	0	4.778772	0.238403	0.182828
24	6	0	3.473717	-1.779557	0.327039
25	6	0	5.887897	-0.506028	-0.203560
26	1	0	4.852980	1.323866	0.274253
27	6	0	4.581309	-2.525059	-0.059900
28	1	0	2.523272	-2.276396	0.532262
29	6	0	5.791593	-1.889634	-0.325066
30	1	0	6.832863	-0.003436	-0.411119
31	1	0	4.500405	-3.608334	-0.153977
32	1	0	6.661180	-2.473773	-0.627260

Sum of electronic and zero-point Energies= -1773.848732
Sum of electronic and thermal Energies= -1773.830951
Sum of electronic and thermal Enthalpies= -1773.830007
Sum of electronic and thermal Free Energies= -1773.899740

Benzyl Carbonotrithioyl Radical
(U)MN12SX/6-311G++(d,p)//(U)MN12SX/6-31G(d)



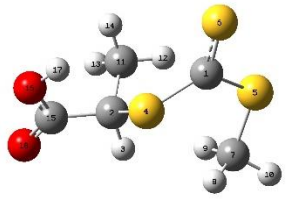
Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-2.344852	-0.130282	-0.000446
2	6	0	0.269738	0.782291	-0.002840
3	1	0	0.003973	1.367923	0.887714

4	1	0	0.006188	1.367941	-0.894037
5	16	0	-0.733679	-0.747122	-0.003868
6	16	0	-2.816020	1.480636	0.001988
7	16	0	-3.688278	-1.142092	0.000985
8	6	0	1.722613	0.394868	-0.000943
9	6	0	2.402983	0.199079	-1.204567
10	6	0	2.399211	0.197396	1.204558
11	6	0	3.742481	-0.173483	-1.203077
12	1	0	1.876265	0.343944	-2.149816
13	6	0	3.738715	-0.175116	1.206708
14	1	0	1.869526	0.340805	2.148382
15	6	0	4.412854	-0.360689	0.002751
16	1	0	4.266054	-0.317188	-2.148323
17	1	0	4.259327	-0.320055	2.153382
18	1	0	5.463839	-0.650520	0.004159

Sum of electronic and zero-point Energies= -1503.218412
Sum of electronic and thermal Energies= -1503.207769
Sum of electronic and thermal Enthalpies= -1503.206825
Sum of electronic and thermal Free Energies= -1503.258149

2-(((methylthio)carbonothioyl)thio)propanoic acid Singlet
(U)MN12SX/6-311G++(d,p)//(U)MN12SX/6-31G(d)



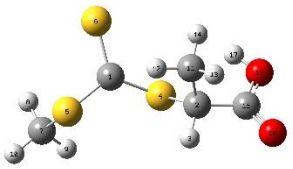
Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	1.428365	-0.464474	-0.119839
2	6	0	-1.294364	0.511776	0.119250
3	1	0	-1.325981	1.547980	-0.234771
4	16	0	-0.161722	-0.496287	-0.925455
5	16	0	2.274080	1.029946	0.188703
6	16	0	2.193111	-1.870303	0.211984
7	6	0	1.277837	2.364454	-0.507734
8	1	0	0.835703	2.072183	-1.467530
9	1	0	0.500654	2.706401	0.186158
10	1	0	1.973534	3.194067	-0.680211
11	6	0	-0.965668	0.449204	1.610692
12	1	0	-0.000977	0.917767	1.838895
13	1	0	-1.746699	0.983568	2.167404

14	1	0	-0.930514	-0.589131	1.966268
15	6	0	-2.727917	-0.013187	-0.066375
16	8	0	-2.901616	-1.337164	-0.084364
17	1	0	-2.048215	-1.806254	-0.093540
18	8	0	-3.655199	0.746298	-0.103430

Sum of electronic and zero-point Energies= -1539.972157
Sum of electronic and thermal Energies= -1539.960217
Sum of electronic and thermal Enthalpies= -1539.959273
Sum of electronic and thermal Free Energies= -1540.011253

2-(((methylthio)carbonothioyl)thio)propanoic acid Triplet
(U)MN12SX/6-311G++(d,p)//(U)MN12SX/6-31G(d)

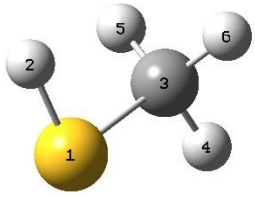


Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-1.194446	0.274036	-0.098896
2	6	0	1.490245	-0.341014	0.544893
3	1	0	1.365075	-1.263146	1.125283
4	16	0	0.248221	-0.339176	-0.835882
5	16	0	-2.351100	-0.703265	0.770636
6	16	0	-1.681784	1.889286	-0.218919
7	6	0	-3.247047	-1.517526	-0.581447
8	1	0	-3.746552	-0.771061	-1.209709
9	1	0	-2.551027	-2.111866	-1.185405
10	1	0	-3.997017	-2.178263	-0.130788
11	6	0	1.369369	0.881812	1.447429
12	1	0	0.396980	0.902429	1.953464
13	1	0	2.156094	0.845335	2.212543
14	1	0	1.477429	1.816133	0.879180
15	6	0	2.897091	-0.392197	-0.053313
16	8	0	3.147444	0.456521	-1.060318
17	1	0	2.335112	0.915435	-1.336555
18	8	0	3.755963	-1.098417	0.396147

Sum of electronic and zero-point Energies= -1539.910101
Sum of electronic and thermal Energies= -1539.897303
Sum of electronic and thermal Enthalpies= -1539.896359
Sum of electronic and thermal Free Energies= -1539.952017

Methanethiol
(U)MN12SX/6-311G++(d,p)//(U)MN12SX/6-31G(d)

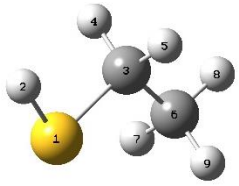


Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	16	0	-0.047841	-0.664263	0.000000
2	1	0	1.284829	-0.819536	0.000000
3	6	0	-0.047841	1.146644	0.000000
4	1	0	-1.097394	1.460291	0.000000
5	1	0	0.432538	1.553794	0.896614
6	1	0	0.432538	1.553794	-0.896614

Sum of electronic and zero-point Energies= -438.588180
Sum of electronic and thermal Energies= -438.584731
Sum of electronic and thermal Enthalpies= -438.583787
Sum of electronic and thermal Free Energies= -438.612229

Ethanethiol
(U)MN12SX/6-311G++(d,p)//(U)MN12SX/6-31G(d)



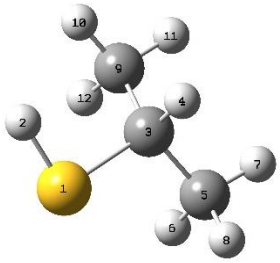
Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	16	0	0.755396	-0.832859	0.000000
2	1	0	2.034333	-0.425599	0.000000
3	6	0	0.000000	0.826415	0.000000
4	1	0	0.331517	1.379007	0.889307
5	1	0	0.331517	1.379007	-0.889307
6	6	0	-1.512646	0.681513	0.000000
7	1	0	-1.859511	0.137850	0.888274
8	1	0	-1.988799	1.670056	0.000000

9	1	0	-1.859511	0.137850	-0.888274

Sum of electronic and zero-point Energies= -477.844585
Sum of electronic and thermal Energies= -477.840031
Sum of electronic and thermal Enthalpies= -477.839086
Sum of electronic and thermal Free Energies= -477.871137

iso-Propylthiol
(U)MN12SX/6-311G++(d,p)//(U)MN12SX/6-31G(d)

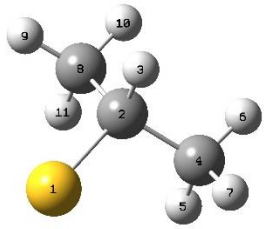


Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	16	0	-1.355408	-0.081616	-0.089725
2	1	0	-1.722988	1.114528	0.399046
3	6	0	0.406392	0.015948	0.407670
4	1	0	0.441163	0.029215	1.507458
5	6	0	1.080354	-1.255714	-0.092029
6	1	0	1.038796	-1.313055	-1.188591
7	1	0	2.136877	-1.262841	0.207774
8	1	0	0.603717	-2.155237	0.317100
9	6	0	1.081339	1.264017	-0.141925
10	1	0	0.602998	2.181719	0.224715
11	1	0	2.137340	1.290917	0.165035
12	1	0	1.040119	1.275106	-1.239234

Sum of electronic and zero-point Energies= -517.104325
Sum of electronic and thermal Energies= -517.098563
Sum of electronic and thermal Enthalpies= -517.097619
Sum of electronic and thermal Free Energies= -517.132741

iso-Propylthiyl Radical
(U)MN12SX/6-311G++(d,p)//(U)MN12SX/6-31G(d)

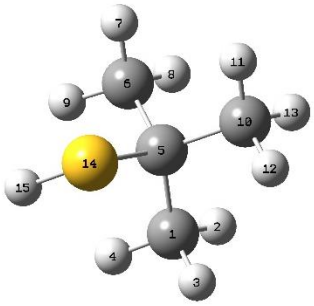


Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	16	0	1.385786	-0.064719	-0.061104
2	6	0	-0.359895	-0.005092	0.415432
3	1	0	-0.416737	0.012138	1.514958
4	6	0	-0.928613	1.312969	-0.120178
5	1	0	-0.876455	1.343080	-1.216821
6	1	0	-1.984333	1.398775	0.174739
7	1	0	-0.391725	2.183295	0.277694
8	6	0	-1.129819	-1.204270	-0.125639
9	1	0	-0.716507	-2.151535	0.242893
10	1	0	-2.182431	-1.150209	0.189378
11	1	0	-1.094421	-1.221683	-1.222860

Sum of electronic and zero-point Energies= -516.471721
Sum of electronic and thermal Energies= -516.466334
Sum of electronic and thermal Enthalpies= -516.465390
Sum of electronic and thermal Free Energies= -516.500553

tert-Butylthiol
(U)MN12SX/6-311G++(d,p)//(U)MN12SX/6-31G(d)



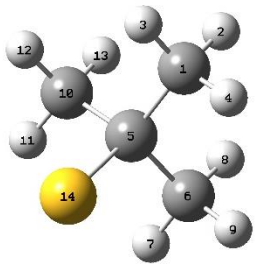
Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-0.839150	-0.720457	-1.255315
2	1	0	-1.939739	-0.735168	-1.272130

3	1	0	-0.485371	-0.216779	-2.163302
4	1	0	-0.491833	-1.762572	-1.285209
5	6	0	-0.345235	-0.005159	0.000001
6	6	0	-0.839154	-0.720423	1.255334
7	1	0	-0.485430	-0.216683	2.163307
8	1	0	-1.939743	-0.735187	1.272112
9	1	0	-0.491791	-1.762522	1.285287
10	6	0	-0.813956	1.449889	-0.000021
11	1	0	-0.457135	1.984510	0.890357
12	1	0	-0.457182	1.984471	-0.890442
13	1	0	-1.912608	1.484248	0.000003
14	16	0	1.498895	0.075355	0.000002
15	1	0	1.703489	-1.253110	-0.000010

Sum of electronic and zero-point Energies= -556.364085
Sum of electronic and thermal Energies= -556.357252
Sum of electronic and thermal Enthalpies= -556.356308
Sum of electronic and thermal Free Energies= -556.393712

tert-Butylthiyl
(U)MN12SX/6-311G++(d,p)//(U)MN12SX/6-31G(d)



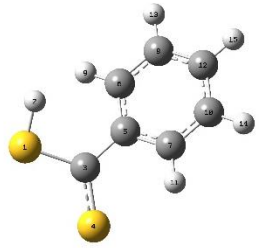
Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-0.857349	1.258766	-0.675672
2	1	0	-1.956379	1.264062	-0.613141
3	1	0	-0.476287	2.164748	-0.188833
4	1	0	-0.580837	1.299726	-1.737595
5	6	0	-0.302470	0.000007	-0.007075
6	6	0	-0.857354	-1.257806	-0.677439
7	1	0	-0.476310	-2.164467	-0.191852
8	1	0	-1.956385	-1.263178	-0.614936
9	1	0	-0.580821	-1.297291	-1.739411
10	6	0	-0.652360	-0.001053	1.487871
11	1	0	-0.260843	-0.893260	1.994007
12	1	0	-0.260848	0.890438	1.995270

13	1	0	-1.747852	-0.001133	1.595900
14	16	0	1.519610	0.000055	-0.079095

Sum of electronic and zero-point Energies= -555.731351
Sum of electronic and thermal Energies= -555.724700
Sum of electronic and thermal Enthalpies= -555.723756
Sum of electronic and thermal Free Energies= -555.761605

Dithiobenzoic Acid
(U)MN12SX/6-311G++(d,p)//(U)MN12SX/6-31G(d)

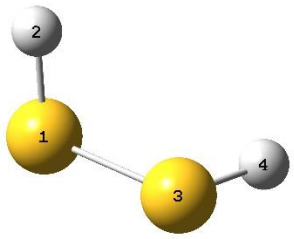


Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	16	0	-2.070656	1.362522	0.339097
2	1	0	-1.059479	2.125126	0.792921
3	6	0	-1.160466	-0.094609	-0.018968
4	16	0	-2.000791	-1.457382	-0.369097
5	6	0	0.319239	-0.024712	-0.004070
6	6	0	1.014383	1.117621	-0.427109
7	6	0	1.050249	-1.146866	0.411313
8	6	0	2.403330	1.135609	-0.431384
9	1	0	0.467184	1.981325	-0.806304
10	6	0	2.437140	-1.115789	0.426308
11	1	0	0.509780	-2.036352	0.734638
12	6	0	3.118704	0.023956	0.004502
13	1	0	2.929774	2.022405	-0.784037
14	1	0	2.991774	-1.989374	0.768938
15	1	0	4.208654	0.043373	0.010295

Sum of electronic and zero-point Energies= -1066.409223
Sum of electronic and thermal Energies= -1066.401257
Sum of electronic and thermal Enthalpies= -1066.400312
Sum of electronic and thermal Free Energies= -1066.442714

Disulfane
(U)MN12SX/6-311G++(d,p)//(U)MN12SX/6-31G(d)

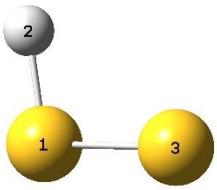


Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	16	0	0.000000	1.031373	-0.055095
2	1	0	-0.946291	1.235656	0.881514
3	16	0	0.000000	-1.031373	-0.055095
4	1	0	0.946291	-1.235656	0.881514

Sum of electronic and zero-point Energies= -797.498338
Sum of electronic and thermal Energies= -797.494960
Sum of electronic and thermal Enthalpies= -797.494016
Sum of electronic and thermal Free Energies= -797.522531

Disulfanyl Radical
(U)MN12SX/6-311G++(d,p)//(U)MN12SX/6-31G(d)

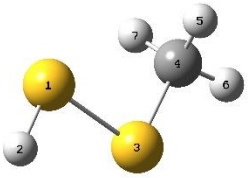


Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	16	0	0.040068	-0.950768	0.000000
2	1	0	-1.282186	-1.242915	0.000000
3	16	0	0.040068	1.028450	0.000000

Sum of electronic and zero-point Energies= -796.887964
Sum of electronic and thermal Energies= -796.884917
Sum of electronic and thermal Enthalpies= -796.883973
Sum of electronic and thermal Free Energies= -796.912870

Methyldisulfane
(U)MN12SX/6-311G++(d,p)//(U)MN12SX/6-31G(d)

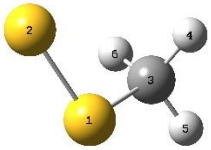


Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	16	0	-1.313648	0.330928	0.000015
2	1	0	-2.067374	-0.781479	-0.000009
3	16	0	0.514938	-0.739336	-0.000009
4	6	0	1.570192	0.718740	-0.000011
5	1	0	1.412207	1.325813	0.898005
6	1	0	2.601212	0.351902	-0.000045
7	1	0	1.412160	1.325846	-0.897996

Sum of electronic and zero-point Energies= -836.744909
Sum of electronic and thermal Energies= -836.740120
Sum of electronic and thermal Enthalpies= -836.739176
Sum of electronic and thermal Free Energies= -836.772600

Methyldisulfanyl Radical
(U)MN12SX/6-311G++(d,p)//(U)MN12SX/6-31G(d)

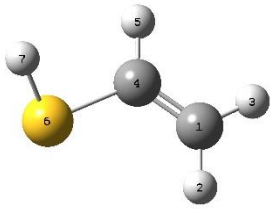


Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	16	0	-0.371214	-0.677296	0.000000
2	16	0	1.345442	0.285827	0.000000
3	6	0	-1.644644	0.612499	-0.000001
4	1	0	-1.548650	1.237251	-0.895598
5	1	0	-2.622203	0.114257	-0.000208
6	1	0	-1.548930	1.237007	0.895800

Sum of electronic and zero-point Energies= -836.147116
Sum of electronic and thermal Energies= -836.142858
Sum of electronic and thermal Enthalpies= -836.141914
Sum of electronic and thermal Free Energies= -836.174998

Ethenethiol
(U)MN12SX/6-311G++(d,p)//(U)MN12SX/6-31G(d)

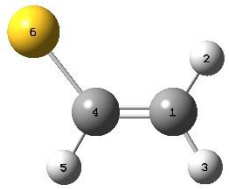


Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	1.671330	-0.257649	0.037302
2	1	0	1.620087	-1.338434	0.166500
3	1	0	2.661298	0.187377	-0.051435
4	6	0	0.581214	0.500826	-0.025197
5	1	0	0.652511	1.582527	-0.153946
6	16	0	-1.049961	-0.171373	-0.039000
7	1	0	-1.649777	0.851436	0.590243

Sum of electronic and zero-point Energies= -476.644344
Sum of electronic and thermal Energies= -476.640340
Sum of electronic and thermal Enthalpies= -476.639396
Sum of electronic and thermal Free Energies= -476.670098

Ethenethiyl Radical
(U)MN12SX/6-311G++(d,p)//(U)MN12SX/6-31G(d)



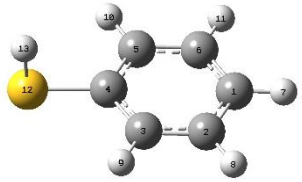
Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	1.284761	1.056711	0.000000
2	1	0	2.094345	0.328809	0.000000
3	1	0	1.560051	2.109402	0.000000
4	6	0	0.000000	0.702200	0.000000
5	1	0	-0.785222	1.468309	0.000000

6	16	0	-0.661109	-0.903749	0.000000

Sum of electronic and zero-point Energies= -476.012163
Sum of electronic and thermal Energies= -476.008566
Sum of electronic and thermal Enthalpies= -476.007622
Sum of electronic and thermal Free Energies= -476.038207

Benzenethiol
(U)MN12SX/6-311G++(d,p)//(U)MN12SX/6-31G(d)

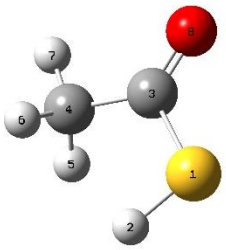


Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	2.287875	0.000036	0.014026
2	6	0	1.590741	-1.204708	0.004525
3	6	0	0.199068	-1.207409	-0.010931
4	6	0	-0.501390	-0.000029	-0.007590
5	6	0	0.199007	1.207375	-0.010994
6	6	0	1.590687	1.204741	0.004473
7	1	0	3.377993	0.000058	0.023594
8	1	0	2.132349	-2.150954	0.005523
9	1	0	-0.353286	-2.146876	-0.026350
10	1	0	-0.353386	2.146819	-0.026376
11	1	0	2.132241	2.151018	0.005484
12	16	0	-2.289366	-0.000051	-0.074700
13	1	0	-2.501975	0.000717	1.252268

Sum of electronic and zero-point Energies= -630.167698
Sum of electronic and thermal Energies= -630.161722
Sum of electronic and thermal Enthalpies= -630.160778
Sum of electronic and thermal Free Energies= -630.197745

Ethanethioic *S*-acid
(U)MN12SX/6-311G++(d,p)//(U)MN12SX/6-31G(d)

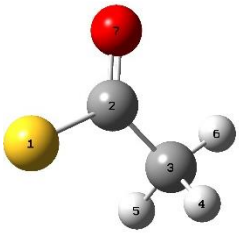


Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	16	0	1.319858	-0.073322	0.000006
2	1	0	1.253877	-1.413752	-0.000081
3	6	0	-0.453214	0.231752	-0.000010
4	6	0	-1.353795	-0.980935	0.000007
5	1	0	-1.167163	-1.599795	-0.887076
6	1	0	-1.167201	-1.599726	0.887137
7	1	0	-2.394067	-0.641009	-0.000034
8	8	0	-0.850140	1.365317	-0.000003

Sum of electronic and zero-point Energies= -551.869125
Sum of electronic and thermal Energies= -551.864152
Sum of electronic and thermal Enthalpies= -551.863207
Sum of electronic and thermal Free Energies= -551.897001

Thioacyl Radical
(U)MN12SX/6-311G++(d,p)//(U)MN12SX/6-31G(d)



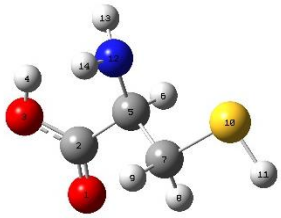
Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	16	0	-1.316621	-0.227234	0.000000
2	6	0	0.395299	0.213524	0.000001
3	6	0	1.416834	-0.887018	0.000000
4	1	0	1.289751	-1.521386	0.886818
5	1	0	1.289740	-1.521388	-0.886815
6	1	0	2.419313	-0.445441	-0.000006

7	8	0	0.649291	1.395615	0.000000

Sum of electronic and zero-point Energies= -551.236845
Sum of electronic and thermal Energies= -551.232087
Sum of electronic and thermal Enthalpies= -551.231143
Sum of electronic and thermal Free Energies= -551.265383

Cysteine
(U)MN12SX/6-311G++(d,p)//(U)MN12SX/6-31G(d)

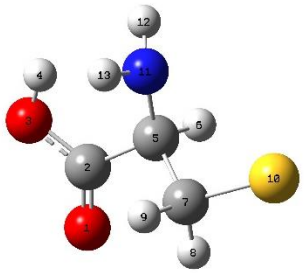


Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	8	0	-1.843383	-1.534858	-0.155371
2	6	0	-1.615282	-0.357388	-0.079613
3	8	0	-2.573283	0.525146	0.228602
4	1	0	-2.177380	1.412403	0.252036
5	6	0	-0.213540	0.230875	-0.352308
6	1	0	-0.045270	0.112084	-1.434715
7	6	0	0.813104	-0.637575	0.371552
8	1	0	0.672398	-1.678817	0.063752
9	1	0	0.647439	-0.582315	1.458242
10	16	0	2.487898	-0.056569	-0.043034
11	1	0	3.081313	-1.247346	0.137109
12	7	0	-0.008413	1.622298	-0.038116
13	1	0	-0.389815	2.306866	-0.682579
14	1	0	-0.108533	1.888351	0.937886

Sum of electronic and zero-point Energies= -721.627989
Sum of electronic and thermal Energies= -721.619900
Sum of electronic and thermal Enthalpies= -721.618956
Sum of electronic and thermal Free Energies= -721.660931

Cysteine Thiyl Radical
(U)MN12SX/6-311G++(d,p)//(U)MN12SX/6-31G(d)

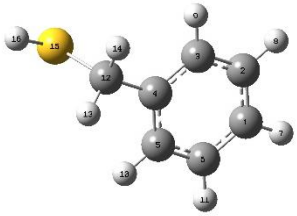


Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	8	0	-1.763924	-1.547144	-0.129873
2	6	0	-1.561970	-0.363547	-0.082673
3	8	0	-2.549725	0.505118	0.170561
4	1	0	-2.182160	1.403986	0.176402
5	6	0	-0.165658	0.242903	-0.332567
6	1	0	0.021621	0.133602	-1.412270
7	6	0	0.875147	-0.602079	0.403457
8	1	0	0.727870	-1.663454	0.148650
9	1	0	0.732436	-0.518738	1.492782
10	16	0	2.543738	-0.146877	-0.059904
11	7	0	0.022922	1.638269	-0.001795
12	1	0	-0.365422	2.312163	-0.655670
13	1	0	-0.170524	1.887137	0.966342

Sum of electronic and zero-point Energies= -720.997933
Sum of electronic and thermal Energies= -720.990240
Sum of electronic and thermal Enthalpies= -720.989296
Sum of electronic and thermal Free Energies= -721.031422

Phenylmethanethiol
(U)MN12SX/6-311G++(d,p)//(U)MN12SX/6-31G(d)



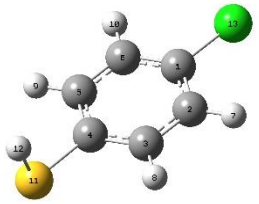
Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-2.649026	0.004107	-0.358387

2	6	0	-1.983490	-1.201845	-0.156858
3	6	0	-0.654076	-1.204337	0.251320
4	6	0	0.023809	-0.003112	0.468010
5	6	0	-0.648634	1.201781	0.253669
6	6	0	-1.977977	1.206725	-0.153476
7	1	0	-3.692311	0.006893	-0.674996
8	1	0	-2.503230	-2.146710	-0.317533
9	1	0	-0.130087	-2.149938	0.404235
10	1	0	-0.119732	2.144441	0.407701
11	1	0	-2.493590	2.154382	-0.311087
12	6	0	1.467234	-0.005759	0.889714
13	1	0	1.693229	0.883785	1.492127
14	1	0	1.692092	-0.897393	1.489593
15	16	0	2.524142	-0.001982	-0.605993
16	1	0	3.700329	0.050895	0.041885

Sum of electronic and zero-point Energies= -669.424746
Sum of electronic and thermal Energies= -669.417191
Sum of electronic and thermal Enthalpies= -669.416247
Sum of electronic and thermal Free Energies= -669.457703

4-Chlorobenzenethiol
(U)MN12SX/6-311G++(d,p)//(U)MN12SX/6-31G(d)



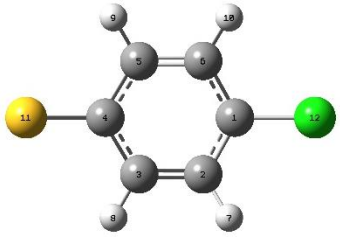
Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-1.397307	-0.000007	0.001510
2	6	0	-0.715202	1.211885	-0.004980
3	6	0	0.675159	1.205472	-0.013898
4	6	0	1.378875	0.000020	-0.007048
5	6	0	0.675188	-1.205433	-0.013948
6	6	0	-0.715182	-1.211875	-0.005022
7	1	0	-1.269343	2.149540	-0.006584
8	1	0	1.222472	2.147767	-0.027036
9	1	0	1.222510	-2.147724	-0.027058
10	1	0	-1.269289	-2.149550	-0.006618
11	16	0	3.164404	0.000027	-0.069180

12	1	0	3.373080	-0.000592	1.258476
13	17	0	-3.136416	-0.000014	0.010354

Sum of electronic and zero-point Energies= -1089.764039
Sum of electronic and thermal Energies= -1089.756921
Sum of electronic and thermal Enthalpies= -1089.755977
Sum of electronic and thermal Free Energies= -1089.796238

4-Chlorobenzenethiyl Radical
(U)MN12SX/6-311G++(d,p)//(U)MN12SX/6-31G(d)

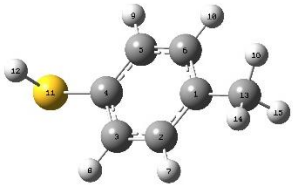


Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	1.340250	0.000014	-0.000010
2	6	0	0.658307	-1.219938	-0.000013
3	6	0	-0.723237	-1.215638	0.000013
4	6	0	-1.453832	0.000005	-0.000018
5	6	0	-0.723249	1.215637	-0.000006
6	6	0	0.658308	1.219944	0.000004
7	1	0	1.219415	-2.153392	-0.000006
8	1	0	-1.275948	-2.154912	0.000030
9	1	0	-1.275933	2.154925	0.000016
10	1	0	1.219380	2.153420	0.000011
11	16	0	-3.164123	-0.000006	0.000004
12	17	0	3.070575	-0.000006	0.000004

Sum of electronic and zero-point Energies= -1089.147126
Sum of electronic and thermal Energies= -1089.140459
Sum of electronic and thermal Enthalpies= -1089.139515
Sum of electronic and thermal Free Energies= -1089.179734

4-Methylbenzenethiol
(U)MN12SX/6-311G++(d,p)//(U)MN12SX/6-31G(d)

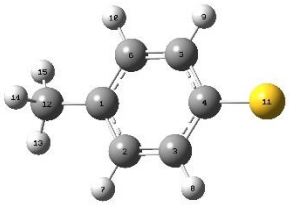


Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	1.820707	0.000127	0.016064
2	6	0	1.102555	-1.198169	0.007647
3	6	0	-0.287567	-1.203702	-0.010580
4	6	0	-0.993414	-0.000010	-0.009148
5	6	0	-0.287720	1.203692	-0.010649
6	6	0	1.102471	1.198287	0.007596
7	1	0	1.642539	-2.147026	0.013821
8	1	0	-0.834664	-2.146430	-0.022360
9	1	0	-0.834878	2.146383	-0.022398
10	1	0	1.642343	2.147200	0.013789
11	16	0	-2.779802	-0.000095	-0.075820
12	1	0	-2.996783	0.000690	1.250685
13	6	0	3.324011	-0.000018	0.000835
14	1	0	3.731936	-0.884659	0.505539
15	1	0	3.708036	-0.007285	-1.029863
16	1	0	3.732039	0.891398	0.493316

Sum of electronic and zero-point Energies= -669.428591
Sum of electronic and thermal Energies= -669.420921
Sum of electronic and thermal Enthalpies= -669.419977
Sum of electronic and thermal Free Energies= -669.460782

4-Methylbenzenethiyl Radical
(U)MN12SX/6-311G++(d,p)//(U)MN12SX/6-31G(d)



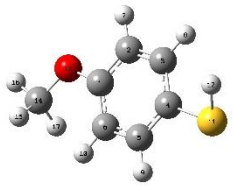
Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-1.760836	0.000160	-0.012270

2	6	0	-1.042691	-1.206291	-0.011054
3	6	0	0.338440	-1.213916	-0.003573
4	6	0	1.071708	0.000012	0.000767
5	6	0	0.338585	1.213956	-0.003568
6	6	0	-1.042621	1.206463	-0.011052
7	1	0	-1.589737	-2.150830	-0.017649
8	1	0	0.891223	-2.153331	-0.004393
9	1	0	0.891409	2.153347	-0.004386
10	1	0	-1.589540	2.151067	-0.017647
11	16	0	2.782300	-0.000079	0.006505
12	6	0	-3.259771	-0.000055	0.014393
13	1	0	-3.673418	-0.886610	-0.482832
14	1	0	-3.629983	-0.007546	1.051396
15	1	0	-3.673637	0.893189	-0.470430

Sum of electronic and zero-point Energies= -668.812415
Sum of electronic and thermal Energies= -668.805194
Sum of electronic and thermal Enthalpies= -668.804250
Sum of electronic and thermal Free Energies= -668.844972

4-Methoxybenzenethiol
(U)MN12SX/6-311G++(d,p)//(U)MN12SX/6-31G(d)



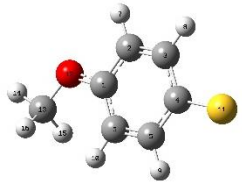
Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-1.378078	0.278579	-0.001551
2	6	0	-0.544915	1.401951	-0.009183
3	6	0	0.830060	1.253694	-0.022207
4	6	0	1.407797	-0.021406	0.006493
5	6	0	0.574109	-1.135146	0.022791
6	6	0	-0.812387	-0.995683	0.006165
7	1	0	-1.005968	2.388773	-0.018050
8	1	0	1.465354	2.139778	-0.055664
9	1	0	1.008364	-2.134690	0.056820
10	1	0	-1.433200	-1.889421	0.016658
11	16	0	3.167105	-0.268764	-0.048709
12	1	0	3.497018	0.769718	0.735245
13	8	0	-2.709793	0.532774	-0.000391
14	6	0	-3.582471	-0.565714	0.003286

15	1	0	-3.448772	-1.187934	0.902679
16	1	0	-4.595272	-0.151240	0.001280
17	1	0	-3.447551	-1.194606	-0.891268

Sum of electronic and zero-point Energies= -744.603395
Sum of electronic and thermal Energies= -744.594929
Sum of electronic and thermal Enthalpies= -744.593985
Sum of electronic and thermal Free Energies= -744.636793

4-Methoxybenzenethiyl Radical
(U)MN12SX/6-311G++(d,p)//(U)MN12SX/6-31G(d)

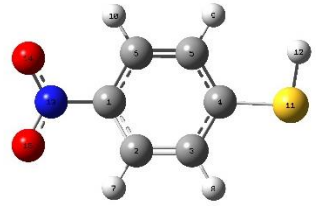


Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-1.318761	0.277119	-0.000001
2	6	0	-0.485305	1.411132	0.000000
3	6	0	0.880355	1.263044	0.000000
4	6	0	1.483886	-0.025805	0.000000
5	6	0	0.618068	-1.147969	-0.000001
6	6	0	-0.757020	-1.009305	-0.000001
7	1	0	-0.956776	2.393051	-0.000001
8	1	0	1.530201	2.138470	0.000001
9	1	0	1.064262	-2.142475	-0.000002
10	1	0	-1.387184	-1.896570	-0.000001
11	16	0	3.178458	-0.218185	0.000001
12	8	0	-2.637962	0.529398	-0.000001
13	6	0	-3.531197	-0.559347	0.000002
14	1	0	-4.535047	-0.125256	-0.000002
15	1	0	-3.403613	-1.182327	-0.898066
16	1	0	-3.403616	-1.182319	0.898077

Sum of electronic and zero-point Energies= -743.989599
Sum of electronic and thermal Energies= -743.981619
Sum of electronic and thermal Enthalpies= -743.980674
Sum of electronic and thermal Free Energies= -744.023362

4-Nitrobenzenethiol
(U)MN12SX/6-311G++(d,p)//(U)MN12SX/6-31G(d)

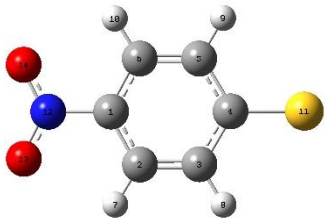


Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-1.118046	0.000074	0.000014
2	6	0	-0.442760	-1.215737	-0.000007
3	6	0	0.941381	-1.212541	-0.000033
4	6	0	1.647325	-0.001476	-0.000029
5	6	0	0.943837	1.209701	-0.000043
6	6	0	-0.441368	1.213902	-0.000017
7	1	0	-1.008052	-2.145258	0.000086
8	1	0	1.482767	-2.158636	-0.000119
9	1	0	1.481123	2.158016	-0.000008
10	1	0	-1.005063	2.144476	-0.000091
11	16	0	3.405666	-0.079512	0.000012
12	1	0	3.615864	1.244340	0.000313
13	7	0	-2.569494	0.002236	0.000023
14	8	0	-3.139298	1.088583	0.000004
15	8	0	-3.142332	-1.082324	0.000014

Sum of electronic and zero-point Energies= -834.584664
Sum of electronic and thermal Energies= -834.576304
Sum of electronic and thermal Enthalpies= -834.575359
Sum of electronic and thermal Free Energies= -834.618562

4-Nitrobenzenethiyl Radical
(U)MN12SX/6-311G++(d,p)//(U)MN12SX/6-31G(d)



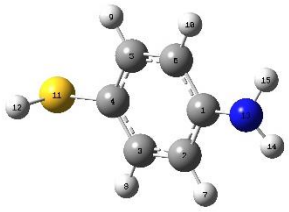
Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z

1	6	0	0.000000	0.000000	-1.059869
2	6	0	-0.000001	-1.224339	-0.393439
3	6	0	0.000000	-1.219790	0.988461
4	6	0	0.000000	0.000000	1.711719
5	6	0	0.000000	1.219790	0.988461
6	6	0	0.000001	1.224339	-0.393439
7	1	0	-0.000001	-2.148541	-0.967366
8	1	0	0.000001	-2.156585	1.544845
9	1	0	-0.000001	2.156585	1.544845
10	1	0	0.000001	2.148541	-0.967366
11	16	0	0.000000	0.000000	3.425770
12	7	0	0.000000	0.000000	-2.519457
13	8	0	-0.000006	-1.085881	-3.086403
14	8	0	0.000006	1.085881	-3.086403

Sum of electronic and zero-point Energies= -833.950200
Sum of electronic and thermal Energies= -833.942173
Sum of electronic and thermal Enthalpies= -833.941229
Sum of electronic and thermal Free Energies= -833.983957

4-Aminobenzenethiol
(U)MN12SX/6-311G++(d,p)//(U)MN12SX/6-31G(d)



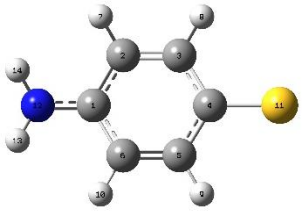
Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	1.840009	-0.000002	0.011934
2	6	0	1.122621	-1.204143	0.002430
3	6	0	-0.263972	-1.200439	-0.011213
4	6	0	-0.977349	0.000002	-0.007091
5	6	0	-0.263968	1.200444	-0.011211
6	6	0	1.122622	1.204142	0.002427
7	1	0	1.663585	-2.151840	0.008055
8	1	0	-0.807087	-2.145597	-0.027175
9	1	0	-0.807086	2.145599	-0.027167
10	1	0	1.663594	2.151835	0.008038
11	16	0	-2.758762	-0.000001	-0.076411
12	1	0	-2.992120	0.000007	1.248289
13	7	0	3.226027	-0.000002	0.087394

14	1	0	3.678665	-0.839204	-0.261448
15	1	0	3.678664	0.839207	-0.261431

Sum of electronic and zero-point Energies= -685.484445
Sum of electronic and thermal Energies= -685.477063
Sum of electronic and thermal Enthalpies= -685.476119
Sum of electronic and thermal Free Energies= -685.516059

4-Aminobenzenethiyl Radical
(U)MN12SX/6-311G++(d,p)//(U)MN12SX/6-31G(d)

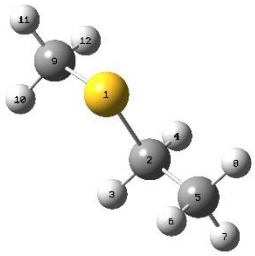


Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-1.781022	0.000003	-0.003717
2	6	0	-1.062538	1.215112	-0.004598
3	6	0	0.312050	1.211219	-0.003034
4	6	0	1.057397	0.000002	-0.000983
5	6	0	0.312050	-1.211215	-0.003035
6	6	0	-1.062532	-1.215107	-0.004598
7	1	0	-1.611481	2.158255	-0.009438
8	1	0	0.862039	2.152452	-0.001224
9	1	0	0.862044	-2.152445	-0.001229
10	1	0	-1.611485	-2.158245	-0.009432
11	16	0	2.759641	-0.000002	0.005498
12	7	0	-3.146864	-0.000006	-0.045901
13	1	0	-3.639871	-0.853789	0.187222
14	1	0	-3.639890	0.853766	0.187221

Sum of electronic and zero-point Energies= -684.873456
Sum of electronic and thermal Energies= -684.866500
Sum of electronic and thermal Enthalpies= -684.865556
Sum of electronic and thermal Free Energies= -684.905461

Ethyl(methyl)sulfane
(U)MN12SX/6-311G++(d,p)//(U)MN12SX/6-31G(d)

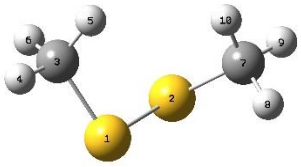


Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	16	0	0.000000	0.814594	0.000000
2	6	0	0.226913	-0.984703	0.000000
3	1	0	-0.265850	-1.409368	0.888079
4	1	0	-0.265850	-1.409368	-0.888079
5	6	0	1.708890	-1.321794	0.000000
6	1	0	2.207836	-0.912414	0.887793
7	1	0	1.855202	-2.409323	0.000000
8	1	0	2.207836	-0.912414	-0.887793
9	6	0	-1.801867	0.863450	0.000000
10	1	0	-2.216564	0.381139	0.895481
11	1	0	-2.109660	1.915398	0.000000
12	1	0	-2.216564	0.381139	-0.895481

Sum of electronic and zero-point Energies= -517.097550
Sum of electronic and thermal Energies= -517.091551
Sum of electronic and thermal Enthalpies= -517.090607
Sum of electronic and thermal Free Energies= -517.126619

1,2-Dimethyldisulfane
(U)MN12SX/6-311G++(d,p)//(U)MN12SX/6-31G(d)



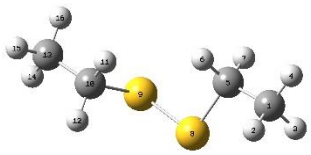
Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	16	0	-0.902429	-0.501967	0.488913
2	16	0	0.902438	-0.501972	-0.488910
3	6	0	-1.805639	0.804795	-0.382753
4	1	0	-2.808457	0.846182	0.061562

5	1	0	-1.326352	1.782814	-0.253797
6	1	0	-1.895747	0.573680	-1.450114
7	6	0	1.805622	0.804816	0.382736
8	1	0	1.895413	0.573820	1.450150
9	1	0	2.808575	0.845962	-0.061295
10	1	0	1.326537	1.782904	0.253535

Sum of electronic and zero-point Energies= -876.008699
Sum of electronic and thermal Energies= -876.002415
Sum of electronic and thermal Enthalpies= -876.001471
Sum of electronic and thermal Free Energies= -876.038793

1,2-Diethyldisulfane
(U)MN12SX/6-311G++(d,p)//(U)MN12SX/6-31G(d)

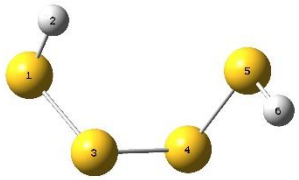


Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	3.219055	0.692622	0.037044
2	1	0	3.230412	0.957122	1.102336
3	1	0	3.765921	-0.251015	-0.085148
4	1	0	3.763627	1.472241	-0.510815
5	6	0	1.798266	0.578237	-0.491096
6	1	0	1.258661	1.528274	-0.371563
7	1	0	1.788972	0.313565	-1.556818
8	16	0	0.925876	-0.727833	0.440006
9	16	0	-0.925871	-0.727830	-0.440008
10	6	0	-1.798269	0.578231	0.491100
11	1	0	-1.258663	1.528269	0.371579
12	1	0	-1.788982	0.313549	1.556819
13	6	0	-3.219060	0.692619	-0.037043
14	1	0	-3.765921	-0.251025	0.085108
15	1	0	-3.763645	1.472214	0.510838
16	1	0	-3.230407	0.957158	-1.102326

Sum of electronic and zero-point Energies= -954.522290
Sum of electronic and thermal Energies= -954.513450
Sum of electronic and thermal Enthalpies= -954.512506
Sum of electronic and thermal Free Energies= -954.556496

Tetrasulfane
(U)MN12SX/6-311G++(d,p)//(U)MN12SX/6-31G(d)

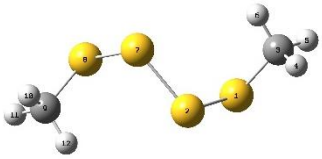


Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	16	0	-2.129561	0.647728	-0.251091
2	1	0	-1.641707	1.738924	0.371221
3	16	0	-0.852827	-0.754709	0.575794
4	16	0	0.871426	-0.778321	-0.563132
5	16	0	2.045597	0.770755	0.145302
6	1	0	2.687533	0.093823	1.118811

Sum of electronic and zero-point Energies= -1593.833369
Sum of electronic and thermal Energies= -1593.827044
Sum of electronic and thermal Enthalpies= -1593.826100
Sum of electronic and thermal Free Energies= -1593.865087

1,4-Dimethyltetrasulfane
(U)MN12SX/6-311G++(d,p)//(U)MN12SX/6-31G(d)



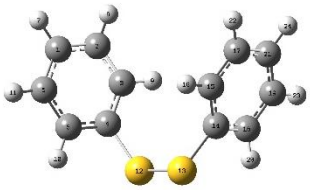
Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	16	0	2.007493	-0.475219	-0.764704
2	16	0	0.668638	-0.803815	0.756012
3	6	0	3.091288	0.771963	-0.026946
4	1	0	3.548740	0.400743	0.897023
5	1	0	3.878068	0.983373	-0.761992
6	1	0	2.535509	1.696774	0.171173
7	16	0	-0.668671	0.804512	0.755364
8	16	0	-2.007467	0.474505	-0.765157
9	6	0	-3.091274	-0.771956	-0.026274
10	1	0	-3.549779	-0.399472	0.896655

11	1	0	-3.877287	-0.985022	-0.761671
12	1	0	-2.535227	-1.696176	0.173887

Sum of electronic and zero-point Energies= -1672.346390
Sum of electronic and thermal Energies= -1672.336912
Sum of electronic and thermal Enthalpies= -1672.335967
Sum of electronic and thermal Free Energies= -1672.382574

1,2-Diphenyldisulfane
(U)MN12SX/6-311G++(d,p)//(U)MN12SX/6-31G(d)

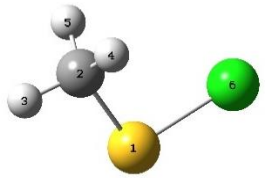


Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-3.189872	1.865518	0.082940
2	6	0	-1.990359	1.971641	-0.615818
3	6	0	-1.230875	0.835015	-0.875883
4	6	0	-1.671137	-0.412607	-0.423678
5	6	0	-2.874528	-0.517669	0.279168
6	6	0	-3.631639	0.621409	0.528440
7	1	0	-3.785954	2.756942	0.280409
8	1	0	-1.645000	2.944586	-0.966335
9	1	0	-0.292408	0.906139	-1.427905
10	1	0	-3.206578	-1.495224	0.629624
11	1	0	-4.571528	0.538076	1.074673
12	16	0	-0.691466	-1.859455	-0.761839
13	16	0	0.619186	-1.855893	0.862135
14	6	0	1.663466	-0.473530	0.452130
15	6	0	1.506720	0.725808	1.150326
16	6	0	2.617984	-0.571510	-0.564567
17	6	0	2.307332	1.821308	0.835485
18	1	0	0.747791	0.795168	1.930417
19	6	0	3.404161	0.528954	-0.882406
20	1	0	2.728057	-1.510553	-1.107744
21	6	0	3.251921	1.724946	-0.181206
22	1	0	2.183499	2.756437	1.382070
23	1	0	4.145751	0.453307	-1.678205
24	1	0	3.873815	2.584993	-0.431326

Sum of electronic and zero-point Energies= -1259.170985
Sum of electronic and thermal Energies= -1259.158825
Sum of electronic and thermal Enthalpies= -1259.157881
Sum of electronic and thermal Free Energies= -1259.211171

Methyl Hypochlorothioite
(U)MN12SX/6-311G++(d,p)//(U)MN12SX/6-31G(d)



Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	16	0	-0.478556	-0.719494	-0.000007
2	6	0	-1.570167	0.708756	-0.000011
3	1	0	-2.591094	0.303438	-0.000354
4	1	0	-1.429987	1.317971	0.900237
5	1	0	-1.429514	1.318629	-0.899742
6	17	0	1.325205	0.254079	0.000002

Sum of electronic and zero-point Energies= -898.170119
Sum of electronic and thermal Energies= -898.165880
Sum of electronic and thermal Enthalpies= -898.164936
Sum of electronic and thermal Free Energies= -898.197422

Chlorine Atom
(U)MN12SX/6-311G++(d,p)//(U)MN12SX/6-31G(d)

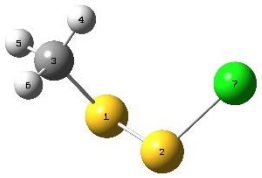
Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	17	0	0.000000	0.000000	0.000000

Sum of electronic and zero-point Energies= -460.113925
Sum of electronic and thermal Energies= -460.112509
Sum of electronic and thermal Enthalpies= -460.111564

Sum of electronic and thermal Free Energies= -460.129602

Methyl Hypochloro(dithioperoxoite)
(U)MN12SX/6-311G++(d,p)//(U)MN12SX/6-31G(d)

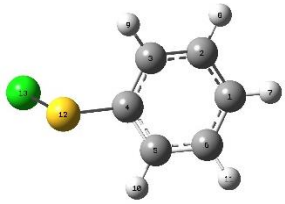


Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	16	0	-1.264652	-0.360651	-0.548938
2	16	0	0.415264	-0.830468	0.446609
3	6	0	-1.961262	0.990286	0.437837
4	1	0	-1.317651	1.876155	0.382351
5	1	0	-2.937744	1.230043	-0.001463
6	1	0	-2.095774	0.684621	1.481055
7	17	0	1.865232	0.548551	-0.167747

Sum of electronic and zero-point Energies= -1296.340269
Sum of electronic and thermal Energies= -1296.334480
Sum of electronic and thermal Enthalpies= -1296.333536
Sum of electronic and thermal Free Energies= -1296.370692

Phenyl Hypochlorothioite
(U)MN12SX/6-311G++(d,p)//(U)MN12SX/6-31G(d)



Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	2.882918	0.150465	-0.361655
2	6	0	2.150973	1.273323	0.020801
3	6	0	0.818183	1.141514	0.389776
4	6	0	0.213261	-0.119806	0.361911
5	6	0	0.945969	-1.244326	-0.028966
6	6	0	2.283513	-1.106162	-0.384564

7	1	0	3.930659	0.257031	-0.644056
8	1	0	2.624761	2.254753	0.038642
9	1	0	0.234633	2.009205	0.698828
10	1	0	0.460029	-2.219815	-0.050099
11	1	0	2.858551	-1.981871	-0.685822
12	16	0	-1.460307	-0.312715	0.897520
13	17	0	-2.500743	0.242006	-0.805978

Sum of electronic and zero-point Energies= -1089.749893
Sum of electronic and thermal Energies= -1089.742701
Sum of electronic and thermal Enthalpies= -1089.741757
Sum of electronic and thermal Free Energies= -1089.783244

5.4 Chapter 4 Experimental Results and Procedures

A. General Photolysis Procedure

Photolysis experiments performed under nitrogen atmospheres were carried out in four-sided quartz cuvettes sealed with rubber septa. Each solution was purged for ten minutes with nitrogen gas and the headspace of each sample was purged for five minutes with nitrogen gas. Samples carried out in air were sealed with a screwcap and were not purged. Samples were irradiated using a Nd:YAG laser operating at 10 Hz using 355 nm light alone, with 355 and 532 nm light, or with 532 nm light alone. The 355 and 532 nm beams were aligned such that, when active simultaneously, the beams were coincident. After photolysis, samples were analyzed by absorption spectroscopy and ^{1}H-NMR.

B. Synthesis of 1-hydroxy-2-methoxyanthracene-9,10-dione (**53**)

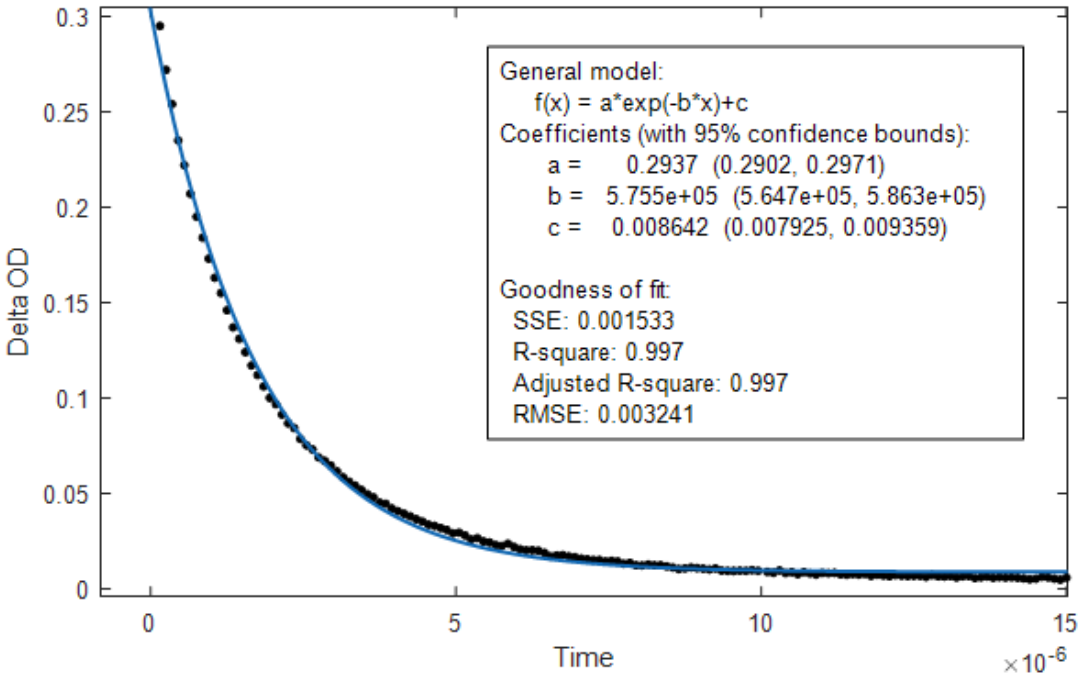
1,2-dihydroxyanthracene-9,10-dione (2.4 g, 10. mmol) and lithium carbonate (1.9 g, 26 mmol) were added to 25 ml of dimethylformamide and stirred for 30 minutes at 60°C. Iodomethane (1.56 ml, 25 mmol) was added slowly and the reaction mixture was left to stir for 24 hours. The reaction mixture was poured into 250 ml of water containing 10% v/v hydrochloric acid. The resulting solution was filtered and the filter cake was rinsed with water until the filtrate was neutral. The filter cake was subsequently dissolved in 3:7 hexanes:ethyl acetate and purified by column chromatography (3:7 hexanes:ethyl acetate). The product was obtained as an orange powder (2.39 g, 94%). m.p.=229-231°C (lit. m.p.=229-230°C).[171]

C. Synthesis of 2-methoxy-9,10-dioxo-9,10-dihydroanthracen-1-yl 4-methylbenzenesulfonate (**54**)

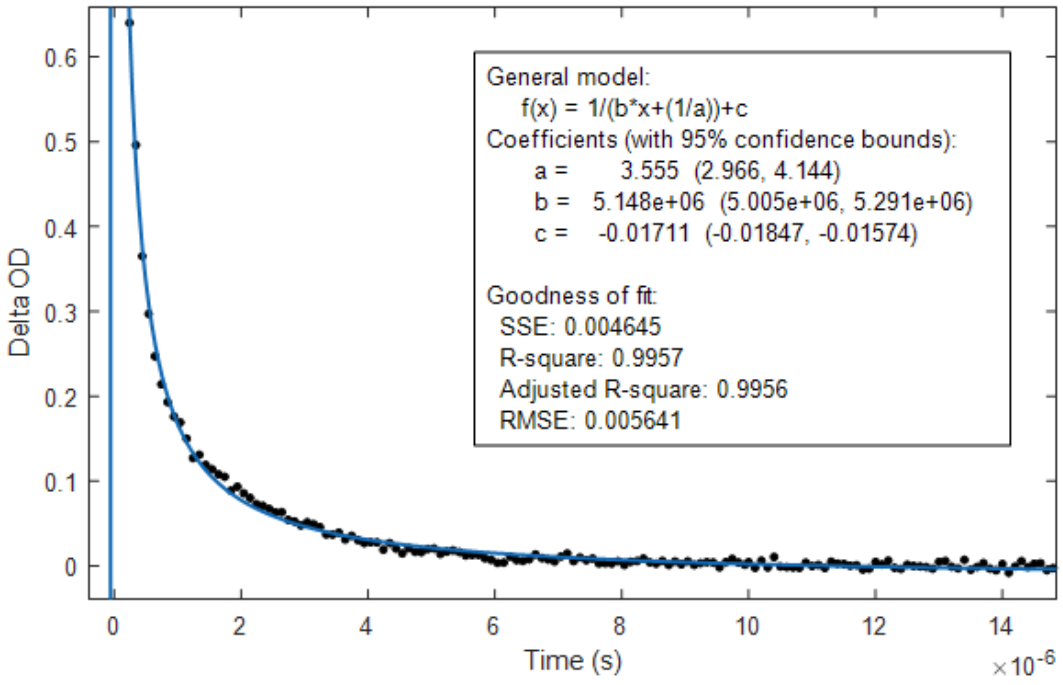
1-hydroxy-2-methoxyanthracene-9,10-dione (0.51 g, 2.0 mmol), 4-methylbenzenesulfonyl chloride (1.4 g, 7.3 mmol), and potassium carbonate (6.6 g, 48 mmol) were dissolved in 38 ml of dry acetone and stirred. After 6 hours, the solvent was removed under reduced pressure and dissolved in ethyl acetate. The liquid was decanted from the insoluble solid and extracted twice with saturate sodium bicarbonate solution and twice with water. The organic layer was dried with magnesium sulfate, filtered, and dried under reduced pressure. The crude product was purified by column chromatography using 10:1 hexanes:ethyl acetate as the mobile phase. After the first fraction was collected, chloroform was added to elute the product.

The solvent was removed under reduced pressure and the product was obtained as a yellow powder (0.31 g, 37%). m.p.=224-225°C.

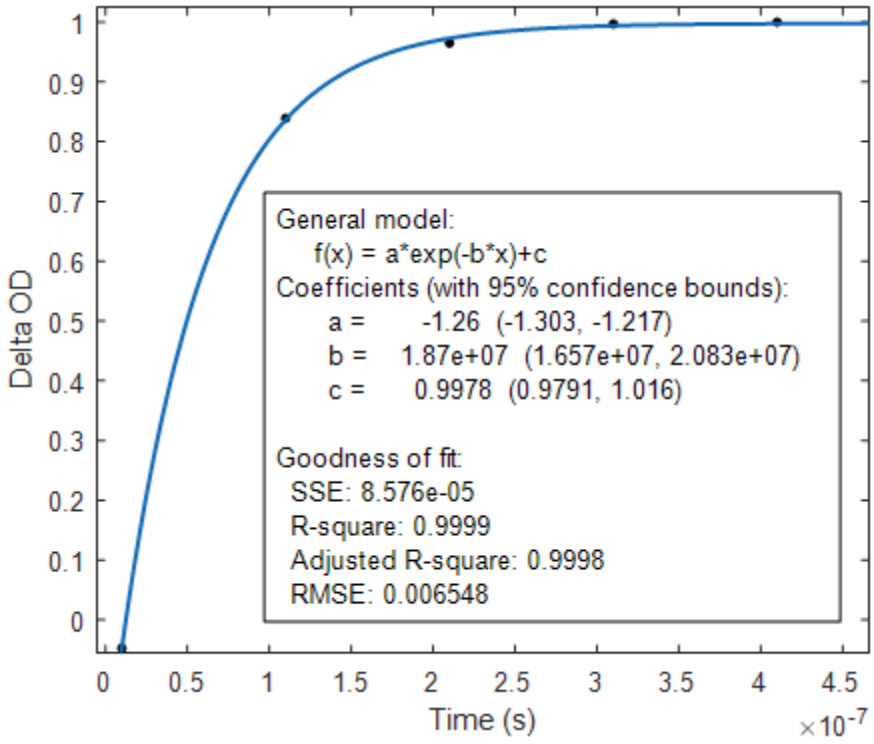
D. Curve fitting for 2-methoxy-9,10-dioxo-9,10-dihydroanthracen-1-yl 4-methylbenzenesulfonate transient at 600 nm



E. Curve Fitting for 2-methoxy-9,10-dioxo-9,10-dihydroanthracen-1-yl acetate transient at 390 nm

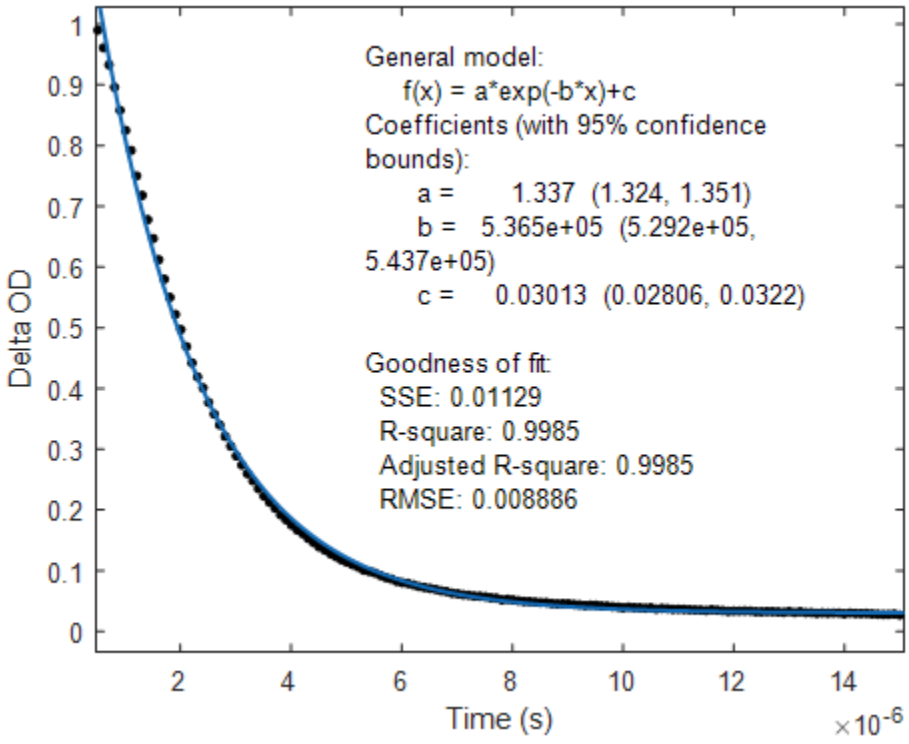


F. Curve fitting for 2-methoxy-9,10-dioxo-9,10-dihydroanthracen-1-yl acetate transient at 480 nm (growth)



G. Curve fitting for 2-methoxy-9,10-dioxo-9,10-dihydroanthracen-1-yl acetate

Transient at 480 nm (decay)



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